GEOLOGIC AND GEOCHEMICAL CONTROLS ON ARSENIC IN GROUNDWATER IN NORTHEASTERN WISCONSIN

A final report prepared for the Wisconsin Department of Natural Resources

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Abstract

This project involved geologic and hydrogeologic approaches to investigate the release of naturally occurring arsenic concentrations to well water in a confined sandstone aquifer in northeastern Wisconsin. Previous work identified sulfide mineralization, concentrated at the contact of the Sinnipee Group and the underlying St. Peter sandstone (Ancell Group), as the primary source of arsenic to the aquifer. Geologic mapping presented in this report indicates a high degree of variability in the distribution of iron-sulfide mineralization at the Sinnipee-St. Peter contact and a high degree of variability of arsenic within the mineralization. Overall, regional trends of increasing arsenic concentration and morphotypes of mineralization occur in outcrops in the St. Peter sandstone from north to south along the Fox River Valley. At a smaller scale, we observed trends of increasing arsenic concentration in the St. Peter sandstone where the sandstone pinches out. Arsenic concentrations in non-mineralized areas of the sandstone average less than 5 parts per million (ppm), while concentrations in mineralized zones vary from 10s to 100s ppm. Alteration of iron-sulfide mineralization is apparently followed by the precipitation of goethite, an iron oxide. In many cases, the iron oxide weathering products of the sulfide mineralization have higher associated arsenic concentrations than the iron-sulfide mineralization.

The St. Peter is also an arsenic-rich formation in areas outside the Fox River Valley, such as the Pine Bluff area west of Madison. This suggests that this sandstone may be a source of arsenic to groundwater in other areas of the state where it is saturated. In the far western portions of Outagamie and Winnebago Counties, to the west of the subcrop of the St. Peter sandstone, arsenic entrained in glacial sediments is a likely source of the arsenic in wells with elevated concentrations.

Hydrogeologic and geochemical characterization of conditions at arsenic impacted wells supports the hypothesis that high (>100 μg/L) levels of arsenic in groundwater occur where the pumping water level in a well is near the elevation of the top of the St. Peter sandstone, because mineralization is subject to oxidizing conditions in well boreholes. This is supported by a correlation to elevated iron and sulfate in groundwater from wells with high arsenic concentrations. Within our study area in the Town of Algoma, two factors affect water levels: variation in topography and stratigraphy that result in lower water levels in the St. Peter, and groundwater withdrawal from increasing numbers of domestic water wells completed in the St. Peter. In either case, lowering the potentiometric surface to the top of the St. Peter likely causes increased oxidation of the mineralized aquifer material.

Arsenic concentrations in groundwater at a field site developed for this project are heterogeneous, varying in zones within the aquifer. Concentrations range from 1 μg/L in a well open to 6.7 m of the aquifer to up to 23 μg/L in a well open to the top of the St. Peter. Groundwater arsenic concentrations correlate to arsenic concentrations in the aquifer materials, suggesting that the local concentration of arsenic in rock is a strong control on the arsenic concentration at a well. Because arsenic concentrations in

the aquifer are heterogeneous, and much of the sandstone hosts very low arsenic concentrations, mixing of water in a fully purged well constructed with a long open interval results in low well water concentrations.

Experiments at the field site indicate that two distinct geochemical mechanisms contribute low (10 μg/L) to moderate (<100 μg/L) arsenic concentrations to well water in this aquifer. Even where the St. Peter sandstone is under confined conditions, oxidation of sulfide minerals may release arsenic to groundwater in zones within the aquifer. Mineral oxidation may have occurred at some time in the geologic past, or current levels of oxygen dissolved in the groundwater may be sufficient to permit slow oxidation to occur. Reductive dissolution of arsenic-bearing iron oxides also appears to contribute low to moderate levels of arsenic to groundwater when the geochemical environment becomes sufficiently more reducing.

We found that the quality of groundwater consumed from wells under typical domestic water use patterns differs from that under fully purged conditions; increasing groundwater residence time correlated to the on-set of strongly reducing conditions and higher arsenic concentrations. We attribute the increase in arsenic in well water under no or low pumping to the reduction of arsenic-bearing iron oxides in the aquifer formation. The well borehole is a microbiologically active environment, and biogeochemical reactions likely contribute to the observed increase in arsenic concentrations. Although well disinfection has the potential to oxidize aquifer sediments, disinfection may be critical at limiting arsenic contamination in settings similar to the field site, where microbes facilitate iron cycling and transformations. Reducing the volume of well bore storage relative to water use may also limit arsenic concentrations in well water.

Because the introduction of oxygen through the borehole and dewatering of the aquifer are not the sole causes of arsenic contamination in wells, preventing further declines in the potentiometric surface will not prevent low to moderate levels of arsenic contamination in this aquifer. Although the reduction of arsenic-bearing iron oxides may release relatively low concentrations of arsenic to well water, this mechanism of release is significant with regard to meeting a drinking water standard of 10 μg/L.

Introduction

Background

In the late 1980s, personnel from the Wisconsin Department of Natural Resources (DNR) investigated wells in the Fox River Valley (FRV) of northeastern Wisconsin containing high concentrations of arsenic. Their work (Burkel, 1993; Burkel and Stoll, 1995; Reiwe et al., 2000) indicated that the contact of the Ordovician St Peter Sandstone (Ancell Group) and Platteville Formation (Sinnipee Group) is the source of high arsenic concentrations in groundwater. Simo et al. (1996; Simo et al.1997) developed stratigraphic and geochemical models of the arsenic occurrence and its release to groundwater in this region. They determined that pyrite and marcasite are the major minerals in a sulfide-bearing secondary cement horizon (SCH) at the base of the Platteville Formation. The SCH contains up to 1.0 weight % arsenic, which is present in solid solution with pyrite and marcasite. The arsenic is also found as a sorbed phase to colloidal-size, iron oxyhydroxide surfaces, suggesting that pyrite/marcasite in the SCH is altering to a nanocrystalline iron oxyhydroxide and that arsenic is sorbing or precipitating onto the hydroxide surfaces.

(Schreiber et al. 2003; 2000) showed that in this area, sulfide oxidation is the likely dominant process controlling arsenic release to highly impacted wells (arsenic concentrations >100 μg/L). This interpretation is based in part on the positive correlation between high arsenic levels in groundwater and the intersection of an arsenic-bearing sulfide cement horizon (SCH) in the aquifer with the static water level in the well (Figure 1). This and other lines of evidence suggest that introduction of oxygen through the well borehole causes oxidation of the sulfide-bearing aquifer material in confined portions of the aquifer. However, as shown in Figure 1, a correlation between the water level in the well and elevation of the SCH is not apparent in many wells with low (1 to 10 μg/L) to moderate (10 to 100 μg/L) arsenic contamination. In the Fox River valley, the St. Peter sandstone aquifer is confined over a large portion of the region, but is unconfined in places, due to dewatering near areas of increased groundwater pumping. Therefore redox conditions are likely variable across the area, becoming more reducing away from unconfined portions of the aquifer.

There are many reports of low to moderate levels of arsenic contamination in aquifers in the mid-western United States (e.g. (Kanivetsky, 2000; Kolker, 2003; Matisoff et al., 1982; Warner, 2001). These concentrations are significant because the U.S. EPA has recently announced a lowering of the drinking water standard for arsenic from 50 to 10 μg/L. This lower standard in turn demands a greater understanding of factors controlling low levels of arsenic release to groundwater supplies. Recent sampling from over 3,300 domestic wells in Outagamie and Winnebago Counties in northeastern

Wisconsin showed that 3% of these wells exceed 50 μg/L arsenic, while a full 17% are impacted at levels between 10 and 50 μg/L (WDNR, 2003).

Project Objectives

The first objective was to investigate geologic controls on the occurrence and magnitude of arsenic in groundwater in the FRV. This portion of the project was designed to characterize arsenic-rich mineralization below the top of the St. Peter sandstone, the spatial variability of arsenic within these mineralized deposits, and the effect of variability in local and regional stratigraphy on the occurrence of arsenic in groundwater in the study area. Our approach was to extensively sample the SCH and other mineralized zones within the Platteville and St. Peter Formations for metals and mineralogical characteristics, map the geographic distribution of the St. Peter, and relate this information to the distribution of arsenic in groundwater.

The second objective was to characterize geochemical and hydraulic conditions that contribute to low- and high-level arsenic impacts in wells. We evaluated regional groundwater geochemistry data from across the FRV for patterns indicative of geochemical mechanisms of release. We also conducted a field study in the Town of Algoma, Winnebago County, to compare and contrast water quality and hydrogeologic conditions at two wells (one with high and one with low arsenic levels). We collected detailed information on the distribution of arsenic in geologic materials and in groundwater at the scale of domestic groundwater withdrawal at one site, where we also performed several experiments to evaluate relationships between water levels, pumping rates, and arsenic concentrations in well water. The hydrogeology and water quality found at this well-characterized field site was then compared to the water quality and hydrogeology at an existing highly-impacted domestic well.

Geochemistry of arsenic release to groundwater

Although industrial, agricultural and mining wastes are potential sources of arsenic contamination to groundwater, the primary source of arsenic to groundwater is naturally-occurring arsenic (Welch et al., 2000). Arsenic is rare in continental crustal materials, but is commonly concentrated in sulfide minerals and hydrous iron oxides (Nordstrom, 2002), which may be present in aquifer sediments. Arsenic in groundwater has been attributed to oxidation of sulfidic aquifer materials (Kinniburgh et al., 1994); Schreiber et al. 2003), release of arsenic from geothermal waters (Welch et al., 1988), evaporative concentration in arid regions (Welch et al., 2000), and desorption or reductive dissolution of arsenic from aquifer materials (Acharyya et al., 2000; Appelo et al., 2002; Kim et al., 2000; McArthur et al., 2001).

In non-geothermal settings, three general geochemical processes govern the release of arsenic to groundwater: oxidation of arsenic-bearing sulfide minerals; desorption of arsenic ions sorbed to aquifer sediments by competitive ions, such as phosphate or bicarbonate; or reductive dissolution of arsenic-bearing mineral oxides. Complicating the identification of a single mechanism of release in a particular environment is that these reactions may be reversible, in chemical disequilibrium, and may be abiotic or microbially mediated. Another dimension of the complexity is added by the spatial variability in the distribution of mineralized deposits, the distribution of arsenic within mineralized deposits, and the variability in the redox conditions across the aquifer.

Oxidation of sulfide minerals can occur via multiple reaction pathways, and may be biotic or abiotic. Primary pieces of evidence for its causing arsenic contamination of groundwater are the presence of arsenic-bearing sulfides and an oxidant. Dissolved oxygen is the most ubiquitous oxidant of reduced compounds in the unsaturated zone and in shallow ground water. Where nitrogen has impacted ground water supplies, nitrate may act as a sulfide oxidant. At lower pH or in the presence of dissolved organic carbon (DOC), dissolved Fe(III) can be a significant oxidant, particularly in the presence of iron-oxidizing bacteria. However, the concentration of Fe(III) is controlled by the oxidation of Fe(II) to Fe(III), which is slow unless, under low pH conditions, it is mediated by iron-oxidizing bacteria (e.g. Nordstrom and Southam, 1997; Schrenk et al., 1998). At the near-neutral pH and low DOC concentrations typically observed in drinking water aquifers, the precipitation of iron hydroxides provides a sink for Fe(III). Therefore, in waters having near-neutral pH, the majority of Fe(III) is expected to be in the solid or colloidal phase and is not expected to act as an agent of sulfide oxidation.

The reaction by-products of sulfide oxidation are distinct; thus, evidence of sulfide oxidation can be found in the chemical signatures of ground water. In aquifers where sulfide oxidation occurs, ground water chemistry should show a positive correlation of arsenic with sulfate, iron, and trace metals contained in the sulfide minerals. Increases in total dissolved solids and specific conductance also result from sulfide oxidation, due to an increase of dissolved ions in the impacted waters. Ground water impacted by sulfide oxidation is expected to have lower pH, provided that there is minimal buffering capacity provided by the host rocks.

The sulfur isotopic signature in sulfide minerals and in sulfate in ground water may also be used to evaluate the occurrence of sulfide oxidation. Although fractionation of sulfur isotopes can occur due to biological and redox cycling (e.g. Kaplan and Rittenberg, 1964), in most cases of sulfide oxidation, minimal fractionation between sulfide and sulfate is observed (Toran and Harris, 1989). This suggests that similar sulfur isotopic signatures in sulfide minerals found within the aquifer and in sulfate from ground water are indicative of these minerals being the source of the dissolved sulfate, and therefore evidence of sulfide oxidation.

While desorption of arsenic from iron and manganese oxides is expected to occur at elevated pH (>8.5), the presence of a competing anion, such as phosphate, bicarbonate, or silicate may also enhance arsenic desorption. The development of strongly reducing conditions at circum-neutral pH may also cause the desorption of arsenic from these mineral oxides, or the reductive dissolution of arsenic bearing iron and manganese oxides (Smedley and Kinniburgh, 2002). Reduction of arsenic from iron-bearing oxides would result in an increase in iron and arsenic concentrations, while sulfate would not increase. Matisoff et al. (1982) reported that reduction of arsenic-bearing iron oxides was a source of arsenic and iron to groundwater in northeastern Ohio. They speculated that a recent lowering of Eh in the aquifer had been caused by the introduction of methane gas or the elimination of oxygenated recharge water.

Procedures and methods

Quarry mapping

We mapped, photographed and sampled outcrops in four quarries to characterize the types of mineralization found at the contact of the Platteville Fm. and the St. Peter sandstone and within the St. Peter sandstone, and to characterize the geometries of the Platteville and St. Peter contact. Leonard, Ben Carrie, Jorgensen and Seymour quarries (Figure 2) were selected for this study based on the thickness of the St. Peter exposure, the extent of three-dimensional outcrops, and the richness in variability of the exposed mineralization. We recorded descriptions of exposures, thickness of units, and the orientation of outcrops. Subsets of 100 rock samples collected from the quarries were used for thin section and microprobe analysis, and whole rock analysis for trace metals. Samples of the St. Peter were also collected in the Pine Bluff area west of Madison, to provide insight into the variability of arsenic content in the St. Peter sandstone on a broader scale.

Rock analysis

Whole rock analysis was performed by Bondar–Clegg, Inc. on 93 samples to determine the concentration of arsenic, iron, sulfur and other elements. Samples were crushed, pulverized, and digested prior to analysis by inductively coupled plasma spectrometry. A limited number of samples were analyzed by atomic absorption to improve detection limits. Characterization of the mineralogical phases in the samples and the location of arsenic in the mineral phase were evaluated using optical petrographic microscope, electron microprobe, scanning electron microscope (SEM), and transmission electron microscopy (TEM) at the UW-Madison Department of Geology and Geophysics. Precipitate collected from downhole monitoring equipment at the Honey Creek field site was analyzed by SEM fitted with an automated American Nuclear Systems EDS system at Department of Geological Sciences at Virginia Tech.

Regional geology and water quality mapping

We used about 275 well constructor records (WCRs) and WGNHS geologic logs to construct a structure map of the Precambrian basement in northeastern Wisconsin. We also constructed maps of the thickness and top elevation of the Ancell Group, using 830 WCR and geologic records and considering mapping of the St. Peter Formation by (Mai and Dott1985).

We present an analysis of two regional groundwater quality data sets in this report. Data used in conjunction with the geologic mapping was provided by Dave Johnson of the WDNR, from town-based residential well arsenic sampling programs conducted in Winnebago and Outagamie counties in 2000 and

2001. Additional data sets collected under similar programs were obtained from the Central Wisconsin Groundwater Center for Fond du Lac County. Homeowners participating in these programs were supplied with a pre-acidified sample bottle, and were instructed to bypass treatment and filtration devices and to purge their water systems for five minutes prior to sampling. The actual sampling procedure used by each homeowner was not verified, although we did remove from the data set multiple samples collected from the same household and samples that were noted to be collected downstream of treatment systems. We determined the location of 3,432 sampled wells by matching the street addresses of participating residences to parcel location. Well locations for the Fond du Lac data set were provided by the Central Wisconsin Groundwater Center. The data set was simplified for contouring by using a moving average scheme to calculate the average arsenic concentration within a circle with a radius of 250 meters.

We selected the data used to characterize regional groundwater quality from the WDNR Groundwater Retrieval Network (GRNs) database. Samples were collected by WDNR personnel, and thus, field sampling procedures are assumed to largely conform to WDNR protocol. Procedures for sampling from water supply wells include sample collection from a cold-water tap situated prior to in-line treatment systems and purged for 3 to 5 minutes. Samples for cation and metals analysis are preserved with nitric acid. In all cases, arsenic was analyzed using ICP-AES or ICP-MS at laboratories certified by the State of Wisconsin. Detection limits ranged from 0.6 to 3 μg/l. Analyses of other water quality parameters also followed standard procedures and were conducted at certified laboratories. Because samples were typically collected for assessment of drinking water quality, samples were not filtered, and the reported metals concentrations represent total concentrations. Information on redox conditions of regional ground water used in this section of the report was compiled from other sources (Batten and Bradbury, 1996; Pelczar, 1996; Saad, 1996; Siegel, 1989; Weaver and Bahr, 1991).

Well installation and hydrogeologic characterization

We collected three 7-cm cores from a 115-m^2 area referred to as the Honey Creek field site (Figure 3) using water-based coring methods to minimize introduction of oxygen to the formation. The friable nature of the sandstone limited the depth of coring. The purpose of boring SB-1 was to verify the presence of arsenic-bearing SCH at the field site prior to well installation; this boring was drilled to 26.8 m and then abandoned. In order to replicate conditions at domestic wells in the region, MW-1 was enlarged to15 cm-diameter after coring by air rotary drilling and was developed by air injection through the drill stem. Rotary-wash drilling and low-flow pumping were used to enlarge and develop MW-2 in order to minimize the introduction of air to the aquifer at this location.

Following initial water quality sampling in MW-2, a FLUTe™ multi-level groundwater monitoring system was installed in the well. The FLUTe™ consists of a water-filled, rubber liner that is sealed against the borehole wall by maintaining an excess head in the liner. Formation water flows into ports installed in the liner through a permeable annulus, rising through tubes until it equilibrates with the head at the port. Water samples are collected by purging the tube twice with nitrogen gas, allowing formation water to flow to the surface through a narrower sampling tube. This system, with the liner sealed against the borehole, essentially eliminates borehole storage; water that flows into the sample tube enters directly from the aquifer through the permeable annulus. We selected the depths of the four sample ports in the FLUTe™ based on visual and chemical analyses of the core and cuttings: a mineralized area in the base of the dolomite confining unit (MW-2-1); at the SCH at the contact of the dolomite and the sandstone (MW-2-2); in an area of white sandstone with no apparent mineralization (MW-2-3), and within a muddy facies encountered near the base of the sandstone (MW-2-4). Measurements of depth to water in the tubes give accurate measurements of head at the sample port after the water level in the tube equilibrated. Because of a check valve in the system that prevents backflow into the aquifer, the FLUTe™ cannot be used to collect real-time measurements of response to pumping during a pump test.

We identified principal zones of groundwater inflow and outflow to the MW-1 borehole with a heat pulse flow meter (Paillet et al., 1996). Flow rates measured under non-pumping conditions indicate if natural gradients are sufficient to induce measurable flow in the borehole under ambient conditions. Flow rates measured under pumping conditions provide an estimate of relative inflow along the open borehole, identifying portions of the exposed formation that contribute flow to the well. We estimated hydraulic conductivity of the sandstone from specific capacity test data collected from MW-1 using the method of Bradbury et al. (1985). Head measurements collected in MW-1 and the four ports of MW-2 provided information on vertical hydraulic gradients.

Groundwater sampling and analysis

Water quality was investigated at the Honey Creek site and at a private, domestic water well located about 2 km north of the field site (Figure 3) that has high (>100 µg/L) arsenic. This well, Wisconsin Unique Well Number IG941, was selected because it is typical of wells in the region with higher arsenic concentrations; the pumping water level reported on the WCR indicates that the water level in the well is at a similar elevation as the top of the St. Peter under pumping conditions (Figure 4). This suggests that the SCH is exposed directly to air in this borehole on a regular basis.

Field parameters, including pH, temperature, specific conductance, dissolved oxygen (DO), and oxidation-reduction potential (ORP), were measured with a Hydrolab™ Minisonde 4a submersible water quality sensor and data logger deployed in MW-1. This unit was placed directly above the pump near the base of the well so that the electrodes remained submerged in well water during periods of pumping.

Sensors were calibrated prior to deployment and were checked for drift following recovery of the unit from the well. Field parameters measured at MW-2 and IG941 were collected using a flow-through cell.

Samples for cations and trace metals analysis were filtered to 0.45-µm and preserved with nitric acid in the field. Samples analyzed for anions were unfiltered and unpreserved. All samples were placed on ice for transport to the EnChem laboratory in Madison, Wisconsin. Anions were analyzed using ion chromatography. Cations and trace metals were analyzed with inductively coupled plasma (ICP) or by ICP with mass spectrometry (ICP-MS).

We used the method of Le at al. (2000) to perform on-site separation of As(III) and As(V). Field procedures included filtering the sample to 0.45-µm and preserving an aliquot with nitric acid for analysis for total dissolved arsenic. A silica-based strong anion-exchange cartridge (Supelco 3 mL SAX Ion Exchange Cartridge) was preconditioned with methanol and DI water. A disposable syringe was then used to push 10 to 15 milliliters (mL) of the sample filtrate through the SAX at a rate of 1 to 2 mL per minute. The effluent solution was preserved in nitric acid. The SAX was assumed to be 100% efficient in removal of As(V); the arsenic concentration in the SAX effluent is assumed to be As(III). As(V) is calculated as the difference between the total dissolved arsenic and the arsenic concentration measured in the SAX effluent. The method was tested extensively in collaboration with Dr. Joseph Alstadt of UW-Milwaukee Chemistry Department and was found to be reliable.

Prior to the use of the field speciation method described above, we tested other methods for measuring concentrations of dissolved arsenic species As(III) and As(V). The modified phosphomolybdate method of Murphy and Riley (1962) and Oscarson and others (1980) did not provide us with sufficiently repeatable low detection levels with the available spectrophotometer. Field preservation of the sample with nitric acid or with freezing on dry ice followed by laboratory analysis for As(III) and As(V) by ICP-MS also proved inadequate, due to iron precipitation and likely changes in the oxidation state of the arsenic species. Results from this work are not considered accurate and are not included in this report.

We tested a limited number of groundwater samples for the presence of colloids in the range of 20 to 400 nanometers using ultra-filtration techniques. A 0.4-µm filtered volume of the sample designated for ultra-filtration speciation was collected in argon-purged bottles and preserved with nitric acid. These samples were transported on ice for same-day speciation analysis at the University of Wisconsin-Madison Water Science and Engineering Laboratory. Samples were filtered using 10,000 Dalton tangential flow, ultra-filtration membranes (Hoffmann et al., 2000). Colloidal fraction was determined by subtracting the concentration of analyte in the permeate from the concentration measured prior to ultra filtration. Trace elements were quantified using ICP-MS. Several groundwater samples were also analyzed for sulfide at the University of Wisconsin-Madison Water Science and Engineering Laboratory with a modified methylene blue method.

Samples for microbiological analysis were collected from a sterilized sample port and transported on ice to the Wisconsin State Laboratory of Hygiene for analysis. Heterotrophic plate counts were performed using the plate method with R2A agar. Iron bacteria were measured microscopically in conformance with Wisconsin State Laboratory of Hygiene (2000) and Standard Methods for Examination of Water and Wastewater (1998).

A sample of the SCH from the MW-1 core, and groundwater samples from MW-1 and well IG941, were collected for sulfur isotope analysis. Sulfur isotope analysis was performed at the University of Waterloo Environmental Isotope Laboratory (UWEIL, 1994). Isotope data are reported as permil differences from the Canyon Diablo trilobite.

Experimental tests

We installed a submersible pump and high- and low water level sensors in MW-1 to control the water level in the well. The pump and submersible water quality sensor were placed at the bottom of the well, the low-level sensor was placed two feet above the pump, and the high-level sensor was installed in the upper, cased portion of the well. This configuration assured that at higher pumping rates (those exceeding 57 l/min) the SCH was exposed to air as the water level in the well cycled between the high- and low-level sensors. Pump cycling and water levels were verified during various phases of the project by recording water levels with a pressure transducer and data logger. Water samples were collected from an in-line sample port prior to discharge to the sanitary sewer.

We performed three experiments in monitoring well MW-1 for this project. The purpose of the first experiment, the SCH exposure test, was to determine if significant exposure of the borehole wall to air would result in increased concentrations of arsenic in well water. Presumably oxidation of sulfide minerals exposed in the borehole would increase arsenic concentrations in the well water. During this experiment, the water level in MW-1 was lowered below the SCH for a total of 635 hours over a three-month period. DO, ORP and pH were measured hourly in MW-1 prior to the start of this test to assess background (non-pumping) conditions. Hourly measurements were also collected during a period of rapid pump cycling (about 8 times per hour) during the test, and through a recovery period following pump shut-off.

We conducted the second experiment, the ambient water quality experiment, to evaluate the relationship between residence time in the borehole and arsenic concentration. During this test, the water level in MW-1 remained at a static water level above the SCH, so that the SCH was not exposed to the atmosphere. Borehole water was periodically sampled over a 17-day period for arsenic, iron and sulfate.

During sample collection, a small volume of water was removed at a low pumping rate to purge the discharge line; the water level in the well remained above the SCH during sample collection. In-situ measurements of DO, ORP and pH provided information on borehole redox conditions.

A third experiment, the domestic pumping test, was conducted to evaluate arsenic release under pumping regimes typical of domestic water use. For the purpose of this test, we estimated that a four-person household uses about 1,135 liters per day (lpd) of water, and we assumed that water use occurs primarily during the morning and late afternoon and evening hours. 380 liters of water (about 1.2 well volumes) were pumped from MW-1 every eight hours to simulate these conditions. We used a pumping rate of 38 l/min to reflect the size of submersible pumps installed in domestic wells in this region. In order to begin the test at conditions reflective of aquifer-quality water, the well was fully purged by pumping 10 minutes every hour at 76 l/min for six days prior to the test. The effect of pumping rate and frequency on borehole redox conditions was monitored by collecting DO, ORP and pH measurements during the rapid pumping schedule used to purge the well prior to the test, and during the more infrequent pumping schedule (simulating domestic water use) of the test itself.

Analysis of drawdown from domestic wells

We used a groundwater flow model to simulate drawdown caused by domestic water use at a housing density similar to that in an area within the Town of Algoma. The purpose of the model was to determine if a recent increase in the number of domestic wells completed in the St. Peter sandstone has the potential to cause unconfined conditions to develop in this region. Unconfined conditions would introduce more oxygen to the formation, potentially exacerbating the release of arsenic to groundwater by sulfide oxidation. MODFLOW (McDonald and Harbaugh, 1988), the U.S. Geological Survey modular groundwater modeling code, was used to simulate one-dimensional steady-state flow in a confined aquifer 16.8 m thick with a uniform hydraulic conductivity of 0.6 m/day. The model represents a highly simplified conceptual model of the local groundwater flow system, and is appropriate for calculating drawdown from multiple wells. The model was calibrated by varying constant head boundary conditions to impose a gradient and heads similar to that mapped by Simo et al (1997). Their map depicts static well water elevations in this area and is based on wells that existed prior to 1993. The calibrated model was then used to simulate flow to 467 wells placed in the model domain at locations of homes appearing on aerial photographs from 1997. The wells were pumped at 1135 l/day (300 gallons/day) to simulate the drawdown of water levels in the confined aquifer from the pre-1993 heads. This method for calibrating and predicting drawdowns assumes that the 467 wells represent new pumping from the area since the static water level map was constructed from 1993 data. The density of the wells in the model ranges from 1 to 2 per acre.

Regional Analyses: Results and Discussion

Characterization of mineralization in outcrops

In the study area, mineralization was observed in two main settings: in a conspicuous highly mineralized zone called the Sulfide Cement Horizon (SCH), and below the SCH as disseminated aggregates. Table 1 shows the mineralization classification defined in this study. Figure 5 is a schematic representation of the stratigraphic location and the types of mineralization, and Figures 6a and 6b show these same features in a more complex and realistic way as they appear in outcrop in Leonard Quarry. Data from this portion of the project is attached in appendices A through H.

Overall there are regional trends of increasing arsenic concentration and morphotypes of mineralization southward along the Fox River Valley (Figure 2). Comparing the overall arsenic concentrations in the four quarries and Pine Bluff, Leonard quarry has the most conspicuous mineralization and highest values of arsenic (Appendices D1, D2, E1 and E2). On a smaller scale, a trend of increasing arsenic concentration is apparent towards areas where the St. Peter pinches out. For instance, the N-S wall (2) of Leonard Quarry and the N-S wall (3) of Jorgensen Quarry show increasing mineralization towards the pinch out of the sandstone (Appendix A). However, there is a wide range in As concentration and mineralization types from sample to sample and quarry to quarry, that make generalizations difficult; the specifics of any given site are highly variable. Arsenic concentration in non-mineralized areas of the sandstone is low, with an average of about 4 ppm.

The SCH is present at the contact of the Platteville dolomite and the St Peter sandstone. It consists of arsenic-rich pyrite, marcasite, and iron oxyhydroxides; arsenopyrite is not present. The mineralization zone is irregular in shape and it varies in thickness, reaching up to 2.4 m. In the study area, the SCH is present in Leonard, Jorgensen, and Seymour quarries. It is also present at the Pine Bluff area west of Madison. Four types of mineralization occur in the SCH, classified as A, B, C and D. Samples of types B and C with oxidized rims were sub-classified as types B1 and C1 (Table 1and Figure 5).

Type A is an oxidized massive layer up to 20 cm that is usually continuous along the contact between the St Peter, Glenwood and Platteville formations. It is irregular in shape, sometimes stylolitic, and it crosscuts boundaries between formations. This type of mineralization is observed at the Leonard (Fig 6a), Jorgensen and Seymour quarries, and in the core SB-1 from the Honey Creek field site. In thin section, type A is an irregular band of pyritic cement infilling the intergranular porosity of the well-sorted quartz arenites. This band is surrounded by limonite (probably goethite) (Appendix C). Arsenic concentration in this mineralization type is usually high, reaching values up to 595 ppm, with an average value of 308 ppm in Leonard Quarry and an overall average (all quarries) of 215 ppm. The histogram of mineralization type A in different quarries (Appendix D2) shows the range of concentration values in the samples and the overall tendency of higher values towards the southwest, where Leonard Quarry is located.

Type B consists of contorted gray bands. They are usually less than 5 cm thick and are closely associated and sometimes laterally equivalent with type A; Simo et al. (1996) describe these as mineral "fronts". They were observed in Leonard and Jorgensen quarries. These gray, cemented bands that have a thin rim of oxidation have been subdivided as type B1. In thin sections, type B appears identical to type A, with the exception that quartz grains in type B appear occasionally altered. The range of arsenic concentrations in type B samples is similar to that of type A (in particular the noticeably higher values of type B1), but the average arsenic concentration in type B is lower than type A (Table 1, Appendices D2 and E1). In Leonard quarry, the maximum arsenic concentration for type B and B1 samples is 489 ppm and the average is 278 ppm. The overall average for type B and B1 samples from the four quarries is 188 ppm.

Type C consists of dark-gray pyritic nodules. The nodules are sub-rounded and highly irregular in shape with diameters up to 5 cm. They tend to aggregate, forming, in some cases, extensive layers, such as those found in the Pine Bluff outcrop and the Seymour quarry. Some of these aggregates appear to be filling burrows. Type C becomes more abundant toward the top of St Peter, and is found in Seymour, Leonard and Jorgensen quarries and the Pine Bluff area. Some nodules have an oxidized rim; these have been classified as C1. In thin section, type C consists of pyrite cement filling intergranular porosity. Type C mineralization has the highest arsenic concentrations. The highest arsenic concentration is in an oxidized (type C1) sample from Leonard quarry, at 917 ppm; type C samples from this quarry average 481 ppm. The overall average from the quarries and Pine Bluff area is 326 ppm.

Type D occurs in a sandstone that has a homogeneous dark gray color (Fig. 6a,b) due to evenly distributed, small amounts of pyrite and marcasite cement that does not form concretions or bands. Type D occurs toward the top of St Peter Fm. It is only present in Leonard and Jorgensen quarries. The thin section shows pyrite cement evenly distributed, infilling the intergranular porosity. Arsenic concentrations are on the order of 20 ppm, with an anomalous high value of 71 ppm.

Type E has the same characteristics as mineralization C but is found below the SCH (approximately 2.4 m below the Glenwood-Platteville contact) and in the Ben Carrie quarry, where the SCH is not present. The average As concentration for type E samples is 156 ppm with a maximum of 523 ppm.

Type F consists of incipient pyritic aggregates less than ½ cm in diameter. Thin sections show patches of pyritic cement filling intra-particle porosity and no oxidized rim. As concentrations are relatively low in Type F mineralization, on the order of 10's of ppm.

Relationship between geology and groundwater quality

Maps of Precambrian and Ancell Group surface topography and thickness of the Ancell Group are presented in Figures 7 through 9. A regional interpretation of arsenic concentrations in well water, based on the results of the town-based sampling programs, is shown in Figure 10. Correlations between arsenic concentration and thickness of the Ancell Group, and arsenic concentration and proximity to areas where the Ancell Group thins, were not evident in these data sets. However, the results of sampling and mapping at the Leonard quarry (described above) show that the thickness of, and arsenic concentrations within, the SCH are likely related to the pinch-out of the St. Peter sandstone. We attribute the lack of identifiable relationships between these geologic and groundwater arsenic concentration maps to the low density of the geologic information. For example, in the Town of Algoma, where 730 wells were analyzed for arsenic concentration over a 0.5 km^2 area in the vicinity of the Leonard quarry, the top and bottom elevations of the St. Peter sandstone (and therefore its overall thickness) is only known at 22 locations.

The map of arsenic in well water viewed with respect to a generalized bedrock map of Wisconsin (Ostrom, 1981) (Figure 11) identifies an area located west of the subcrop of the St. Peter and Prairie du Chein formations where arsenic exceeds 10 µg/L in well water. Although well construction records were not identified for the wells that exceeded 10 µg/L, a majority of water wells completed in this area draw water from the shallow sand and gravel aquifer. One potential source of arsenic in this aquifer is arsenic-rich sediment entrained in glacial till.

Regional groundwater quality

The information and analysis in this section, prepared as a part of this project, was published earlier in Schreiber et al. (2003). Ground water quality data used in this section of the report were obtained from the WDNR GRNS database system. The samples were collected by WDNR for a variety of purposes (e.g., routine monitoring, studies designed to assess arsenic impacts, and studies focusing on other water quality issues). Thus, each well was not analyzed for the same constituents. In addition, because some wells are open to more than one hydrogeologic unit, the results may reflect differences between aquifers, rather than between waters affected by reactions with the SCH. However, comparison of the data to studies of regional water quality aids in evaluating the water chemistry of arsenic-impacted wells with respect to background ground water.

We considered four types of water: non-impacted (arsenic below detection limit), low (greater than the detection limit and less than 10 µg/l As), moderate (10-100 µg/l As), and high (greater than 100 µg/l As). Typical of water quality data, the data set is censored and as such, the concentrations reported for most constituents are not normally distributed (Gibbons, 1994). Because of this limitation, box plots

(Figure 12) are used to evaluate and compare the water quality results. The distributions of concentrations were compared for iron, sulfate, pH, alkalinity, nickel, zinc, manganese and specific conductance. The box plots should be viewed with consideration of sample size, which is indicated on the figure.

The data set for non-impacted ground water in this study (Figure 12, Type A) is generally in agreement with studies of regional ground water quality (Saad, 1996; Siegel, 1989; Weaver and Bahr, 1991). The notable exception to this is the elevated sulfate, which on the basis of the 73 wells included in the WDNR database, has an average concentration of 169 mg/l and ranges up to 1100 mg/l. Further examination of the data set shows that a majority of wells with elevated sulfate concentrations are municipal supply wells open to both the St. Peter and the deep sandstone aquifer. An area of relatively saline groundwater is present in the vicinity of Lake Winnebago (Ryling, 1961) and is a likely source of the elevated sulfate levels in these wells. The few shallow wells that exhibit elevated sulfate levels and no detectable arsenic are located in the eastern portion of Brown County, where the source of sulfate may be gypsum dissolution from the overlying shale confining unit (Saad, 1996; Weaver and Bahr, 1991).

Ground water with low (<10 µg/l) concentrations of arsenic (Figure 12, Type B) has similar chemistry to non-impacted ground water, with pH ranging from 7 to 8, iron concentrations less than 10 mg/l, and sulfate concentrations below 200 mg/l. Although alkalinity concentrations have a similar range as the non-impacted water, the low-arsenic wells display a higher median concentration. The box plots of manganese, zinc, and to a lesser extent, nickel, show higher maximum concentrations for the low arsenic wells than for the non-impacted wells. However, values for both data sets are within the same order of magnitude.

In wells with moderate (10-100 µg/l) arsenic concentrations (Type C), iron, pH, alkalinity, as well as nickel, manganese and zinc, appear elevated above background. Although moderate-arsenic wells show different water quality from non-impacted wells, sulfate concentrations are within the range observed for non-impacted water.

In contrast, ground water with high (>100 µg/l) arsenic concentrations (Type D) exhibits a distinctly different chemical signature than non-impacted water. Sulfate is notably higher, reaching concentrations over 3000 mg/l. Iron concentrations, which range up to 1000 mg/l, are significantly higher than those measured in moderate, low, or non-impacted water. The box plots also illustrate the low pH associated with the high levels of arsenic, with values dropping to a minimum of 2.1. Levels of nickel, manganese and zinc in the high-arsenic wells are orders of magnitude greater than non-impacted wells. The increase in concentrations of ions increases the specific conductance, and specific conductance ranges from 1000 to 7000 µmhos/cm. Alkalinity levels are similar to those in the low- and moderate-arsenic wells.

Field Study: Results and Discussion

Study Area

The investigation focused on the Honey Creek field site, located at the edge of an area of widespread and variable groundwater arsenic concentrations in the Town of Algoma, approximately five km. west of Oshkosh (Figure 3). This figure also shows the location of private well IG941. Regional hydrostratigraphy includes glacial and glaciolacustrine sediments overlying a thick sequence of Paleozoic sedimentary rocks (Schreiber et al. 2000). In the vicinity of the Honey Creek site and well IG941, 9 to 14 m of unlithified deposits, varying from clay to sand and gravel, overlie 13 to 23 m of Sinnipee dolomite. The St. Peter sandstone is variable in thickness, ranging from about 15 to over 22 m (Figure 4). The elevation of the water table is variable across the study area, present in the upper bedrock at higher elevations and in clayey surficial deposits at lower elevations. Domestic wells are typically cased into the Sinnipee, and constructed with boreholes open to the base of the dolomite and St. Peter sandstone. According to static and pumping water levels reported on well construction records, the St. Peter sandstone is under confined conditions across the area but is locally dewatered due to pumping.

Distribution of arsenic in aquifer materials

At the Honey Creek site, the SCH is present at the base of the Sinnipee dolomite and top of the St. Peter sandstone. A 0.5 cm-thick band, similar to the type A mineralization identified in quarries, is present at the tope of the SCH. Veins and nodules of sulfide mineralization were scattered throughout the cores obtained from the upper 4.5 m of the St. Peter (Figure 13a). An orange-colored rind, presumed to be an iron oxide coating on some of the mineralization, was present at the time of core recovery (Figures 13b and 13c). A majority of the sandstone appears oxidized with a white-pink to red color. Arsenic concentrations in the mineralized zones range from 23 to 585 mg/kg (Table 2 and Appendix I). Portions of the sandstone below the SCH are white-pink to red in color, also suggesting iron-oxide coating on the quartz grains. The whole rock arsenic concentration in this material is less than 20 mg/kg. Other zones within the sandstone are light to dark gray in color, suggesting reduced iron is present. Although texturally similar to the white-pink sandstone, the gray sandstone has an arsenic content of 90 mg/kg. Mineralized veins and nodules found within the oxidized sandstone have arsenic concentrations similar to that of the SCH, ranging from 161 to 585 mg/kg. Mineralized veins are also present in the dolomite directly overlying the SCH, with levels of arsenic ranging from 23 to 73 mg/kg. Although drilling was not performed for this project at private well IG941, the detailed geologic characterization conducted at the Leonard quarry, located about 800 m east of IG941 (Figure 3) showed that the thickness of the type A mineralization within the SCH is highly variable in this region, ranging up to 20 cm in the quarry walls.

Honey Creek Site hydrogeology

The clayey surficial deposits and the Sinnipee dolomite confine the St. Peter sandstone. The water table is about 1 m below ground surface at the Honey Creek site, with a downward vertical gradient of approximately 0.3 from the water table to the sandstone. Within the sandstone, vertical gradients are negligible under non-pumping conditions (Figure 14). There is little to no exchange of water between the borehole and the aquifer under non-pumping conditions; natural gradients are not sufficient to induce measurable flow into and out of the borehole. The regional horizontal gradient in the sandstone is about 0.001 to 0.005 the northeast (Conlon 1998; Simo et al. 1997).

Contribution to well yield at MW-1 is primarily from the sandstone and flow to the well from the dolomite is low. Flow meter logging showed that under pumping conditions, the flow rate in MW-1 is relatively constant from the bottom of the well upwards. These patterns are consistent with observations made during coring that extensive fracturing in the dolomite is limited to the upper two meters of the formation. The horizontal hydraulic conductivity of the sandstone is about 0.6 to 0.9 m/day, while the hydraulic conductivity of the overlying, unfractured Sinnipee dolomite is expected to be two to three orders of magnitude lower (Batten et al., 1999). Although pumping from MW-1 induces vertical hydraulic gradients within the St. Peter, pumping rates up to 95 l/min do not result in extensive dewatering of the sandstone aquifer; the St. Peter remained fully saturated at MW-2 (4.6 m from the pumping well) for the duration of this project (Figure 15).

Honey Creek site groundwater chemistry

Groundwater in the St. Peter sandstone at the site is Ca-Mg-HCO_3 type, and has about 0.25 mg/L DO, with ORP slightly reducing at –28 mV and a pH of 7.1. Prior to the three experiments, arsenic concentrations in samples from MW-1 ranged from less than 3.7 μg/L to 15.5 μg/L, with the higher concentration present in a sample of borehole water (Table 3). (To simplify description of the data set, samples collected under fully purged conditions are referred to as "aquifer water" and samples collected under stagnant or partially purged conditions as "borehole water".) Concentrations of other trace metals (e.g., Ni, Mo, Co, Zn), which are positively correlated with arsenic in highly impacted wells in the FRV (Schreiber et al. 2003), are low in this aquifer water.

Similar to MW-1, the arsenic concentration was below the detection limit in aquifer water sampled from MW-2 prior to installation of the multilevel monitoring system. However, after the multi-level system was installed, arsenic was detected in the aquifer water collected from each of the four monitoring ports. Arsenic concentrations measured at each port were consistent over the 8-month period of this study

(Figure 16), and the relative magnitude of the arsenic concentration among the four ports correlates to the whole rock arsenic concentrations in aquifer material from similar elevations (Table 4).

Results of samples of borehole and aquifer water from MW-1 collected for ultra-filtration analysis were consistent with other sampling at this well, in that the borehole water has higher concentrations of arsenic, iron, manganese, and zinc than does the aquifer water (Table 5). The ultra-filtration analysis also shows that 33% of the arsenic in the borehole water is colloidal, while only 3% of the arsenic in the aquifer water is colloidal. In both water types, almost all (>99%) of the iron is colloidal. This suggests that within the borehole, dissolved phase arsenic sorbs to colloidal iron.

Sulfur isotope data show similar signatures in rock (sulfide) and water (dissolved sulfate) samples from the site. The sulfur isotopic signature ($\delta^{34}S$) of pyrite from the SCH sample collected from the MW-1 core was 2.93 permil. The $\delta^{34}S$ of sulfate in groundwater from MW-1 was 2.87 permil, and 2.34 permil in a second sample that was collected after much of the experimental pumping at the well was completed.

Although dissolved organic carbon (DOC) in borehole and aquifer water is less than 1 mg/L, microbial activity in MW-1 borehole was evaluated because of the hydrogen sulfide odor noticed at the wellhead following extended periods of non-pumping. Borehole water was positive for heterotrophic bacteria (300 per ml) and for the presence of sulfate reducing bacteria. A low number of iron oxidizing bacteria, *Gallionella* (14 per ml), were detected; *Leptothrix* and *Crenothrix*, other iron oxidizers commonly found in wells, were not present. A black coating that precipitated on the down-hole water quality sensor during an extended period of non-pumping in MW-1 was determined by SEM/EDS to be an iron oxide. Although quantitative analysis of the crystal structure has not been conducted, the black color and the strong magnetic properties of the precipitate suggest that it is magnetite. Sulfur was not detected in the precipitate.

Effects of pumping on water chemistry

The SCH exposure experiment was conducted over a three-month period. Samples of aquifer water and borehole water collected during the test showed a range in arsenic concentration from 1.1 to 22 µg/L (Figure 17). Iron concentrations ranged from 0.01 to 1.5 mg/L, and sulfate varied from 13 to 16 mg/L. Increases in these constituents did not appear related to increased time of borehole exposure to air, however concentrations of arsenic and iron were consistently higher in borehole water samples than they were in aquifer water (Table 3).

Redox conditions measured during background (non-pumping) conditions, rapid pump cycling (about 8 times per hour) during the test, and through a recovery period following pump shut-off, show that in contrast to the reducing conditions in the borehole during background and recovery periods, during pump cycling conditions are moderately oxidizing (Figure 18). Similarly, DO was below detection limit

(0.2 mg/L) during background conditions, was often elevated during pump cycling, but returned to less than 0.2 mg/L soon after the recovery period began. pH was higher during both background and recovery periods than it was during pump cycling. The higher pH in borehole water is attributed to buffering from the Sinnipee dolomite that is exposed in the borehole and remains saturated under non-pumping conditions. This monitoring suggested that redox conditions change rapidly in the well water, and subsequent monitoring was conducted at a shorter time interval.

Results from the ambient water quality experiment show that arsenic concentrations in the well increase during non-pumping periods (Figure 19). Over the 17-day test, concentrations of arsenic in borehole water increased from 1.1 to 16 μg/L. The iron concentration also increased, but sulfate remained relatively consistent. Hydrogen sulfide odor was noticeable in the discharge water during sample collection. Strongly reducing conditions developed rapidly in the borehole under non-pumping conditions (Figure 20). The pH of the borehole water increased from 7.4 to 7.8 over the first nine days of the test, which is attributed to buffering from the dolomite exposed in the well.

During the domestic pumping experiment, arsenic concentrations varied but were generally low (Table 6). Arsenic concentrations in samples collected at the beginning of pumping cycles (less than 0.5 well volumes purged) on days two and 14 of the test were both slightly greater than 6 μg/L. Samples collected later in a pumping cycle, at purge volumes of 0.6 and 1.3 borehole volumes, respectively, contained arsenic at 2.9 and 2.7 μg/L. The arsenic was predominantly arsenite in all samples collected during the domestic pumping test, which may be significant in terms of toxicity to humans (NRC 1999).

The lower pumping rate and frequency of the domestic pumping test induced more strongly reducing conditions than the higher pumping rate and frequency of well purging prior to the test (Figure 21). During the purge period, the borehole water equilibrated at about –50 mV ORP and DO remained at about 0.5 mg/L. Spikes in ORP and DO can be seen at the on-set of pumping each hour; the water level in the well was drawn down 15.2 m during this hourly pumping cycle, exposing the aquifer formation to air. Under the domestic pumping schedule, DO was 0.25 mg/L, and ORP was –100 mV and falling when the meter was removed from the borehole. ORP increased with the on-set of pumping each eight hours, but DO did not. We attribute this to the smaller amount of drawdown (7.6 m) induced under the domestic schedule, which does not introduce air to the formation. The pH of the borehole water remained between 7.3 and 7.4 under the both pumping regimes.

Water quality at well IG941

Samples collected at well IG941 that have elevated arsenic also have increased concentrations of iron, sulfate, nickel, manganese and molybdenum (Table 7). Arsenic is primarily As (V) at this well, which is consistent with the more oxidizing conditions measured in this well water compared to that at

MW-1. Ultra-filtration of samples from the well showed that first draw and purged samples from this well have about 5% colloid-associated arsenic, although arsenic concentrations in both the first draw and purged samples collected on this data are orders of magnitude lower than those typically detected in this well water (Table 5). The well may have been relatively well-purged prior to the sampling event due to the occupants of the residence being home on this day. The $\delta^{34}S$ of sulfate in groundwater from this well, 2.05 permil, is slightly lower than that found at MW-1. Groundwater at the well has higher ORP (+270 mV) and higher DO (0.82 mg/L) than water at the field site. pH is 7.1 at IG941.

Analysis of drawdown

We used a groundwater flow model to assess drawdowns caused by domestic wells completed in the St. Peter sandstone in an area within the Town of Algoma (Figure 22). Model results (Figure 23) indicate that at this well density, drawdowns on the order of 15 m are likely to occur in the St. Peter sandstone. Based on the water levels recorded at the Honey Creek field site, this amount of drawdown would be sufficient to cause dewatering of the sandstone in the vicinity of the development.

Discussion

Arsenic release in the aquifer

Groundwater arsenic concentrations are spatially heterogeneous within the 115-m^2 scale of the field site, and correlate to the local distribution of arsenic within the rock and mineral assemblages identified in the core. Although the point concentrations of arsenic in MW-2 ports are elevated (7 to 23 µg/L), aquifer water collected from the long open-intervals of MW-1 and MW-2 (prior to FLUTe™ installation) are less than 3 µg/L, indicating that mixing of moderate- and low-arsenic waters from zones within the aquifer results in dilution of higher point concentrations. Domestic wells in this region impacted by high arsenic concentrations probably have a locally large volume of high-arsenic aquifer solids; wells with low arsenic concentrations may benefit from the mixing of aquifer water permitted by long, open boreholes.

The upper two ports of MW-2, which were positioned to sample water from mineralized zones in the dolomite and at the SCH, have higher arsenic concentrations (21 and 23 µg/L) than do the deeper ports (7 and 12 µg/L), which sample water from non-mineralized zones lower in the sandstone. Whole rock data show less arsenic (<12 mg/kg), iron (<2 weight %) and sulfur (<1 weight %) in cuttings recovered from these deeper intervals. While this may be due in part to mixing of materials in the cuttings collected from the deeper intervals, it also suggests that the form of the arsenic-bearing mineral and the distribution of solid-phase arsenic in the aquifer materials within the immediate vicinity of a well are significant controls on the arsenic concentration in that well.

Evidence from the field site suggests that oxidation of sulfides within the St. Peter aquifer has occurred in the past, and is likely still occurring. The similarity of the sulfur isotopic signature in sulfide of the SCH and dissolved sulfate in aquifer water indicates that the sulfide is the likely origin of the sulfate. The weathered rind present on mineralized zones in the core and the detection of iron oxides in the SCH show that oxidation of sulfide minerals has occurred; the presence of this weathered rind at the time of core collection suggests that oxidation took place prior to this project. The whole rock chemistry data show that several samples of aquifer solids with elevated arsenic have a notable lack of sulfur relative to iron (Table 1), which is also suggestive of sulfide oxidation. As the arsenic-bearing sulfides are oxidized, iron oxide weathering products are formed. Once released from sulfides, arsenic, which has a high affinity for iron oxides, may sorb to the oxides, resulting in portions of the aquifer matrix having elevated iron and arsenic but low sulfur.

A source of oxidant must be present in the aquifer for sulfide oxidation to occur. Lower water table conditions may have been prevalent in this area during the last intra-glacial period, prior to the deposition of glacial till in near-by bedrock valleys, providing an opportunity for regional oxidation of the St. Peter sandstone (personal communication, T. Hooyer). Results from the four ports of MW-2 suggest that even where the aquifer is currently under confined conditions with DO at about 0.25 mg/L, arsenic can reach moderate levels. Oxygen introduced through the borehole or dewatering of the aquifer, suggested by Schreiber et al. (2000) to be sources of oxygen at wells in the FRV with high arsenic concentrations, is not a trigger of arsenic release at MW-2. Air introduced at MW-2 during drilling and well installation was limited, and pumping at MW-1 over the course of the project did not cause dewatering of the aquifer at MW-2. Arsenic levels in MW-2 ports did not increase over time (Figure 16), providing additional evidence that changes in geochemistry and redox conditions induced by experiments conducted at MW-1 were limited to the immediate vicinity of the MW-1 borehole. The role of oxidants other than DO at this site is unlikely; nitrate is below detection level and, at the circumneutral pH of this groundwater, ferric iron is not a likely oxidant. If sulfide oxidation is indeed occurring in the aquifer at the field site, the reaction may be slow due to the relatively low DO and may also be passivated by precipitation of iron oxide weathering products on the sulfide surface.

The water level and water quality information from well IG941is consistent with regional data that show a coincidence between water levels and the elevation of the SCH at highly impacted wells (Figure 1) and with elevated sulfate and iron levels at highly impacted wells (Figure 12). The water quality IG941 is distinct from that at MW-1 and MW-2. At IG941, where arsenic is typically on the order of several hundred μg/L, iron <u>and</u> sulfate, as well as other trace metals, are also elevated. Due to changes in topography and thickness of stratigraphic units, the potentiometric surface (as measured in wells open to the Sinnipee Dolomite and the St. Peter sandstone) is 8 m above the top of the St. Peter at IG941 compared to 14 m at MW-1 and MW-2. The static and pumping water levels at IG941 indicate that the water level in the well is likely routinely fluctuating above and below the SCH. This, in conjunction with the water quality data and the more oxidizing conditions measured in the well water, suggests that sulfide oxidation is currently occurring in the vicinity of this well. The low arsenic, iron and sulfate detected in the well when samples were collected for ultra-filtration suggests that the sulfide oxidation and subsequent release of arsenic, iron and sulfate to well water is a local phenomena that occurs at the borehole, and when a relatively large volume of water is removed from the well, groundwater which has not had significant residence time near the borehole shows improved water quality. One factor that was not evaluated during this study is the thickness of, and concentration of arsenic within, the SCH at IG941. The results from MW-2 showing a correlation between arsenic concentration in rock and groundwater suggest that IG941 is located in an area where the SCH is relatively thick and arsenic rich.

Redox conditions and arsenic release in the borehole environment

Changes in redox conditions occur as groundwater moves from the aquifer into the well borehole. Differences in the geochemical environments of aquifers and wells are documented in the literature of well performance and biofouling (Taylor et al., 1997; Tuhela et al., 1993; van Beek and van der Kooij, 1982). Conditions unique to the well include gas-water interactions occurring at the air-water interface; changes in redox related to pump action, which introduces oxygen into well water, and the growth of microorganisms that can facilitate a variety of biogeochemical reactions, including iron-precipitation and sulfate reduction. Each of these interactions is known to occur in wells and has the potential to affect arsenic behavior.

While the MW-1 borehole was subjected to atmospheric oxygen for 635 hours during the SCH exposure experiment, this introduction of oxygen does not appear to have caused an increase in arsenic in the well water from sulfide oxidation. Arsenic concentrations in MW-1 measured during and after the SCH exposure test are not substantially higher than the 15 µg/L measured in borehole water prior to the start of the test. Had significant weathering of minerals exposed in the borehole wall occurred during the SCH exposure test, water quality data from the end of this test and from the ambient water quality experiment would be expected to reflect the geochemical signature of more extensively weathered minerals.

The geochemical environment in the MW-1 borehole becomes strongly reducing during periods of non- and low- pumping. Although low-flow rate pumping triggers a short-term increase in ORP with each pump cycle, conditions remain reducing (Figure 21). The overall higher DO and ORP levels resulting from the high flow rate used to purge the well is attributed to oxygenation of borehole water as the water level rises and falls over 15 m each hour, which both agitates the water column and introduces air directly to the formation.

These results suggest that the increase in arsenic and iron in borehole water under non- and low-pumping conditions is related to the more reducing environment in the borehole, and may be caused by reduction of arsenic-bearing iron oxides that are exposed in the borehole wall. Following a period of extended pumping, the borehole presumably fills with the low-arsenic water from the St. Peter aquifer. The borehole water becomes strongly reducing within two days of pump shut-off (Figure 20), coincident with an increase in arsenic and iron concentrations (Figure 19). While arsenic and iron are higher in borehole water than in aquifer water, the concentration of sulfate does not increase (Figure 19). An increase in sulfate would be expected if sulfide oxidation is the direct cause of arsenic and iron release to the borehole water. While the hydrogen sulfide odor noticed in borehole water suggests that sulfate reduction occurs in the borehole, the concentration of sulfide measured in aquifer and borehole water was less than 1 µg/L, indicating that reduction to sulfide is not a major sink for sulfate in the borehole.

Although counts of iron-reducing bacteria were not conducted, the presence of sulfate-reducers within the borehole demonstrates that redox conditions are favorable to microbial reduction of iron oxides. Iron reduction is energetically more favorable than, and is generally expected to occur prior to, sulfate reduction (Lovely, 2000). Although iron reduction can occur abiotically, this reaction pathway would be relatively slow; the presence of iron-reducing bacteria would explain the relatively rapid rise in arsenic and iron concentrations during the non-pumping test and the maintenance of slightly elevated arsenic concentrations during the domestic pumping test.

The diverse populations of microorganisms found in the well (sulfate-reducing, heterotrophic, and iron-oxidizing bacteria) indicate a complex geochemical environment within the borehole, including both anaerobic and aerobic microenvironments. Although DOC is low in the aquifer water, the presence of these bacterial communities demonstrates that sufficient organic carbon is available in the well to support microbial growth. Contamination from drilling and other down-hole equipment is a likely source of organic carbon to the MW-1 borehole. The presence of some iron-oxidizing bacteria suggest that microbial consumption of oxygen may contribute to the more strongly reducing conditions that develop in the borehole. The precipitation of what appears to be magnetite in the borehole is also suggestive of microbially mediated iron reduction. Work by Lovley et al. (Lovely et al., 1987) has shown that iron-reducing bacteria can induce precipitation of extracellular magnetite under anaerobic conditions. This evidence for microbiological role in arsenic and iron cycling in the borehole suggests that well disinfection may play a critical role in controlling arsenic levels at some wells.

The finding of primarily colloidal iron in the MW-1 borehole is not necessarily consistent with the measurements of a strongly reducing environment, because the presence of colloidal iron suggests that the iron is an oxidized species. Determination of ferrous and ferric iron was not performed during this study. However, reduced iron–sulfide species can form larger aggregates that would also be filtered by the method used here (Dave Krabbenhoft, personal communication, 6 March, 2003). If iron-sulfide species are forming in the well under the strongly reducing conditions, this could be the cause of the high fraction of iron retained by the ultra-filtration method.

Conclusions

The geologic mapping efforts completed during this project indicate a high degree of variability in the distribution of iron-sulfide mineralization at the Sinnipee-St. Peter contact and a high degree of variability of arsenic within the mineralization. An interesting aspect of the regional and quarry mapping is that the alteration of the iron-sulfide mineralization is followed by the precipitation of goethite, which in many cases seems to concentrate higher values of As that the iron-sulfide mineralization. This supports observations of water quality at the field site that suggest reductive dissolution of arsenic-bearing iron oxides is a mechanism of arsenic release to groundwater.

However, the geologic data available is not at a density sufficient to identify relationships between geologic factors and high arsenic concentrations in groundwater. It is clear that elevated levels of arsenic are present in the St. Peter Fm outside the Fox River Valley, such as the Pine Bluff area west of Madison. Arsenic present in glacial sediments may also contribute to groundwater arsenic concentrations in some wells in the western portions of Outagamie and Winnebago Counties.

The hydrogeologic characterization completed at two locations in the Town of Algoma, and the analysis of regional groundwater quality, support the hypothesis that high levels of arsenic in groundwater occur where the pumping water level in a well is near the elevation of the SCH (presumed to be at the top of the St. Peter sandstone), because the mineralization is subject to oxidizing conditions in well boreholes. This is supported by correlations to elevated iron and sulfate concentrations in groundwater from wells with high arsenic concentrations. In contrast to the findings in wells at the field site, sulfide oxidation via lowering of the water level in the borehole is the likely cause of high levels of arsenic contamination at a private well about 2.5 km to the northwest. Water quality at this well is consistent with other highly impacted wells in the region, and is indicative of sulfide oxidation. Arsenic released to groundwater under these conditions is primarily As(V), which may have implications for treatment technologies designed for highly impacted wells. The potentiometric surface of the aquifer is lower at this well due to changes in topography and stratigraphic thickness. The intersection of the water level in this well with the SCH is a result of the topography and stratigraphy and is not a result of over-pumping of the aquifer. However, in areas where the St. Peter is under confined conditions, the density of private domestic water wells constructed in some areas of the Fox River valley is sufficient to lower the potentiometric surface to the top of the St. Peter and potentially cause increasing concentrations of arsenic in well water.

These findings indicate that two distinct mechanisms are contributing low to moderate arsenic concentrations to well water in this confined, sandstone aquifer. In areas where the St. Peter sandstone is under confined conditions, such as the Honey Creek field site, oxidation of sulfide minerals appears to release arsenic to groundwater in zones within the aquifer. The oxidation may have occurred at some time in the geologic past, or current levels of oxygen may be sufficient to permit slow oxidation to occur.

Although the SCH was exposed to atmospheric oxygen for 640 hours during this project, this did not appear to have a significant impact on the well water chemistry. Sulfide oxidation does not appear to have been triggered by the manipulation of the water level in this well. This may be due to the relatively thin layer (< 0.5 cm) of arsenic-rich mineralization at the top of the SCH at the field site.

Reductive dissolution of iron oxides is also a likely contributor of low to moderate levels of arsenic to groundwater at the field site. The domestic pumping experiment demonstrates that the quality of groundwater consumed from wells under typical domestic water use patterns differs from that of aquifer water because of reactions that occur within the well borehole. The borehole is an environment where redox conditions can change rapidly in response to groundwater withdrawal. Changes in redox likely play a significant role in complex cycling of arsenic and iron in the borehole; results from these experiments suggest that well-recognized processes of iron oxide reduction and subsequent precipitation of iron minerals are likely sources and sinks of arsenic within the well borehole. Borehole geochemistry is also affected by biogeochemical reactions because it is an environment conducive to microbiological growth. Although well disinfection has the potential to oxidize mineralized zones in the aquifer, well disinfection may be critical at limiting low to moderate arsenic contamination in wells where microbes facilitate iron transformations and iron oxide reduction. Arsenic released to groundwater under these conditions is primarily As(III), which may have implications for treatment technologies designed for low to moderately impacted wells.

The arsenic concentrations in groundwater at the field site are heterogeneous, varying in zones within the aquifer. The groundwater arsenic concentration correlates to the arsenic concentration in the aquifer materials, suggesting that the local concentration of arsenic in rock is a strong control on the arsenic concentration at a well. Because groundwater arsenic concentrations in the aquifer are heterogeneous, and the arsenic concentration in much of the rock is very low, mixing of waters in a fully purged well constructed with a long open interval results in lower well water concentrations.

Groundwater residence time in wells, and well purge volume, affects water quality. The quality of groundwater consumed from wells under low pumping rates differs from that of the aquifer water. In the particular hydrogeologic setting of the Honey Creek site, sufficient water is removed from the well under simulated domestic water use patterns to provide some dilution of the borehole water quality that develops under the strongly reducing environment in the well under non-pumping conditions. Reducing the volume of well bore storage relative to water use may be useful in controlling low to moderate arsenic concentrations in well water.

Although casing through the uppermost portion of the St. Peter sandstone will prevent oxidation of the high-arsenic SCH typically encountered at the top of the St. Peter, the additional casing will not necessarily prevent low to moderate levels of arsenic release from the biogeochemical reduction of iron oxides within the St. Peter. This is because arsenic-rich iron oxides may be present at low levels throughout the sandstone. Because the introduction of oxygen through the borehole and dewatering of the aquifer are not the sole cause of arsenic contamination in wells, preventing further decreases in the potentiometric surface will not necessarily prevent additional contamination in wells completed in this aquifer. Although the reduction of arsenic-associated iron oxides appears to release lower concentrations of arsenic to well water, contamination at these lower levels is significant because of the new, lower arsenic drinking water standard of 10 μg/L.

Acknowledgements

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Tables

TABLE 1
CLASSIFICATION OF THE MINERALIZATION TYPES

MINERALIZATION TYPES	DESCRIPTION	No. of samples	Avg. As (mg/kg)
A	OXIDIZED MASSIVE LAYER	12	215
B	CONTORTED GRAY SULFIDE BANDS	5	90
B1	CONTORTED GRAY SULFIDE BANDS WITH AN OXIDIZED RIM	5	278
C	NODULAR PYRITIC AGGREGATES	9	297
C1	NODULAR PYRITIC AGGREGATES WITH AN OXIDIZED RIM	1	917
D	HOMOGENEOUS GRAY SULFIDE CEMENT	6	23
E	NODULAR PYRITIC AGGREGATES	14	156
F	INCIPIENT PYRITIC AGGREGATES	3	14
--	NO APPARENT MINERALIZATION	12	4

Table 2
Whole Rock Concentrations of Selected Elements in Aquifer Materials

Location	Depth (m)	Description	As ppm	Cu ppm	Pb ppm	Zn ppm	Mo ppm	Ni ppm	Co ppm	Sr ppm	Mn ppm	Cr ppm	S %	Fe %	Al %	Mg %	Ca %	Na %	K %
SB-1	21.64	dolomite, mineralized veins	73	145	21	13	6	81	46	39	715	26	3.95	4.45	0.08	8.39	13.93	0.04	0.06
MW-1	22.25	dolomite, mineralized veins	23	11	3	7	3	24	9	67	1009	20	1.05	1.71	0.08	10.05	16.59	0.03	0.07
MW-1	23.16	mineralized zone, purple	161	109	53	32	37	154	113	5	387	434	0.02	12.67	0.04	0.04	0.04	0.01	0.01
MW-1	23.47	sandstone, white to gray-brown	1.8	7	7	6	38	14	6	5	153	628	<0.01	2.27	0.02	0.02	0.16	<0.01	0.01
MW-1	23.93	mineralized nodule, purple	510	83	585	56	53	234	196	9	168	632	0.5	21.4	<0.01	0.06	0.04	<0.01	<0.01
MW-2	23.99	sandstone, white	16	7	12	7	32	23	10	18	206	513	0.03	1.54	0.03	2.07	3.43	0.01	0.01
MW-2	24.02	sandstone, orange	13	10	12	55	47	35	10	5	138	764	<0.01	2.55	0.02	0.11	0.18	<0.01	0.01
MW-2	24.14	sandstone, white	2.8	8	7	5	31	12	3	3	56	502	<0.01	0.72	0.02	<0.01	0.02	<0.01	0.01
MW-2	24.51	sand, light gray	8	149	10	61	10	16	6	32	412	107	0.24	1.11	0.15	7.85	11.62	0.03	0.05
MW-2	23.96	SCH	585	129	442	85	29	378	241	20	681	241	17.9	20	0.11	0.25	0.77	0.01	0.02
MW-2	25.3 - 26.5*	sandstone, white	1.8	16	4	10	15	6	2	9	135	232	0.1	0.57	0.04	1.8	3.27	0.01	0.02
MW-2	28.3 - 29.6*	sandstone	<1	3	<2	<1	15	4	2	3	48	218	0.04	0.45	0.02	0.38	0.75	0.01	<0.01
MW-2	29.9 - 31.1*	sandstone	1.9	28	2	15	14	7	3	6	48	208	0.03	0.53	0.02	0.25	0.5	<0.01	0.01
MW-2	31.4 - 32.6*	sandstone	4	13	<2	<1	15	5	3	4	34	214	0.16	0.68	0.03	0.1	0.19	0.01	0.04
MW-2	32.9 - 34.1*	sandstone	<1	11	<2	<1	16	7	3	2	33	243	0.11	0.47	0.02	0.04	0.07	0.01	0.02
MW-2	34.1 - 34.7*	sandstone, muddy matrix	12	67	8	3	17	66	38	47	134	237	0.58	1.37	1.32	1.37	2.53	0.02	0.85

* indicates sample was from drill cuttings and is likely to have more mixing of materials than samples selected from core

Table 3
Selected Water Chemistry Results from MW-1 and MW-2

date	well id	water type	As µg/L diss.	Mo µg/L diss.	Ni µg/L diss.	Zn µg/L diss.	Co µg/L diss.	Mn µg/L diss.	Ca mg/L diss.	Mg mg/L diss.	Na mg/L diss.	K mg/L diss.	Fe mg/L diss.	Cl mg/L total	SO4 mg/L total	Alk as CaCO3 mg/L total	NO3 +NO2 mg/L total	organic carbon mg/L diss.	P mg/L total	Sulfide µg/L total
5/3/01	MW-1	aquifer	<3.7	<1.3	2.0Q	12	0.94Q	45	45	41	9.8	1.7	0.120	3.3	14	270	<0.015			
8/2/01	MW-1	borehole	15.5																	
8/24/01	MW-1	aquifer	5.8						46	41	11	1.4	<0.25	2.9	14	280			<0.1	
8/31/01	MW-1	borehole	22						38	40	14	1.6	0.970	3.2	15	280			<0.1	
9/11/01	MW-1	aquifer	<4.4										0.011		13					
9/27/01	MW-1	borehole	10										1.500		16			0.816		0.054
9/27/01	MW-1	aquifer	<4.4										0.190		15			0.659		0.036
1/21/02	MW-1	borehole	15	2.9	9.9	11	0.55	60					2.900		24					
1/21/02	MW-1	aquifer	2.4	<0.52	1.3	5.8	0.60	47					0.140		33					
4/1/02	MW-1	aquifer	6.4		2.2	12	0.27	46	42	36	8.8	1.7	0.470	4.0	18	280				
5/3/01	MW-2	aquifer	<3.7	5.0	3.6Q	11	6.3	56	60	41	14	3	0.059	5.8	52	270	<0.015			
4/1/02	MW-2-1	aquifer	21		0.75	5.6	0.22	22	36	40	9.8	1.6	0.850	5.2	19	270				
4/1/02	MW-2-2	aquifer	23		0.39	5.2	0.24	22	38	40	9.5	1.5	0.710	5.4	18	280				
4/1/02	MW-2-3	aquifer	7.2		1.2	4.1	0.54	85	55	36	7.6	2.2	0.890	2.5	16	310				
4/1/02	MW-2-4	aquifer	12						64	37	6.7	2.4	1.400	2.4	17	350				

"Q" indicates result was greater than the detection limit but less then the limit of quantification
results reported as dissolved were filtered to 0.45 microns; total indicates sample was not filtered

Table 4

Arsenic in groundwater and aquifer materials at MW-2

Sample port	Depth (m)	Aquifer material at port	As (ug/L)	Whole rock As at similar depth (mg/kg)
MW-2-1	21.3	Sinnipee dolomite	21	73
MW-2-2	24.0	St. Peter sandstone at the SCH	23	585
MW-2-3	25.3	St. Peter sandstone	7.2	1.8
MW-2-4	34.1	St.Peter sandstone, muddy matrix	12	12

Table 5

Ultra-filtration Sampling Results

	As µg/L	Fe µg/L	Mn µg/L	Cd µg/L	Cu µg/L	Zn µg/L	Pb µg/L	S µg/L
MW-1 borehole water								
total dissolved	12.7	3100	127	0.004	0.7	6.51	0.235	5721
%colloidal	33	99	5.8	8	14.4	86	64	3.6
MW-1 aquifer water								
total dissolved	1.73	118.7	46.22	0.0025	3.504	5.86	1.153	5422
%colloidal	3.2	99.5	1.8	0	54	20.5	99	2.8
IG941 aquifer water								
total dissolved	12.9	0.86	65.66	0.0483	14.3	40.6	0.01	9044
%colloidal	5.4	7.5	4	1.8	18	10	0	3.6

Note: results of IG941 borehole water are not reported because the well had been fully purged by the homeowners prior to sampling.

Table 6

Domestic Pumping Test Results

Pumping rate (l/min)	Pump cycling prior to sample collection	Borehole volumes purged	As µg/L	As^{3+} µg/L
76	6 days @ 10 min/hour	0.5	1.8	--
38	2 days @ 10 min/8 hours	0.4	6.3	5.6
38	14 days @ 10 min/8 hours	0.3	6.4	5.6
38	14 days @ 10 min/8 hours	0.6	2.9	2.6
38	14 days @ 10 min/8 hours	1.3	2.7	2.5

Table 7

Water Chemistry Results from Well IG941

date	As	As	As3+	Mo	Ni	Mn	Ca	Mg	Mg	Na	K	K	Fe	Fe	Cl	SO4	Alk (CaCO3)
	ppb total	ppb diss.	diss.	ppb total	ppb total	ppb total	ppm diss.	ppm diss.	ppm total	ppm diss.	ppm total	ppm diss.	ppm diss.	ppm total	ppm total	ppm total	ppm total
5/31/2000*	390	370		<4	1300	230	76		40		1.4			16	1.1	108	275
9/27/2001		<4.4											<0.008			47	
9/27/2001		9.8					77	42		3.5		1.4	<0.008		1.1	24	330
1/21/2002		250	56										11			51	

*sample collected by DNR

Second sample collected on 9/27 was after 20 minutes of purging well. Residents were home that day and low arsenic concentration is attributed to extended period of water use by residents prior to sampling.

Figures

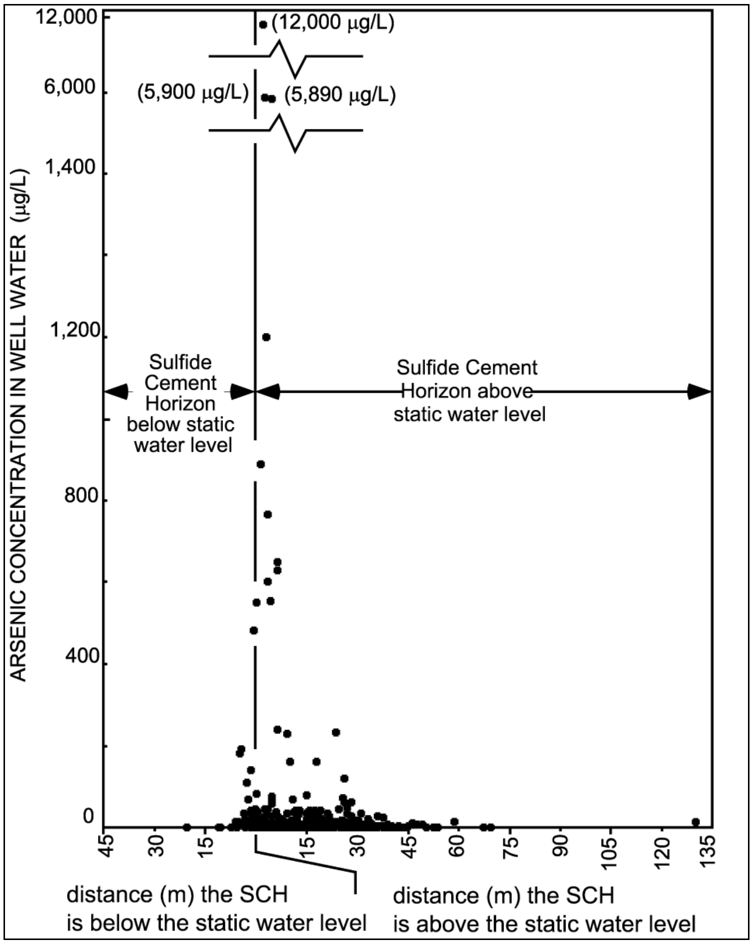

Figure 1. Correlation of high arsenic levels to elevation of SCH and static water level in wells. Re-printed from Schreiber et al 2003.

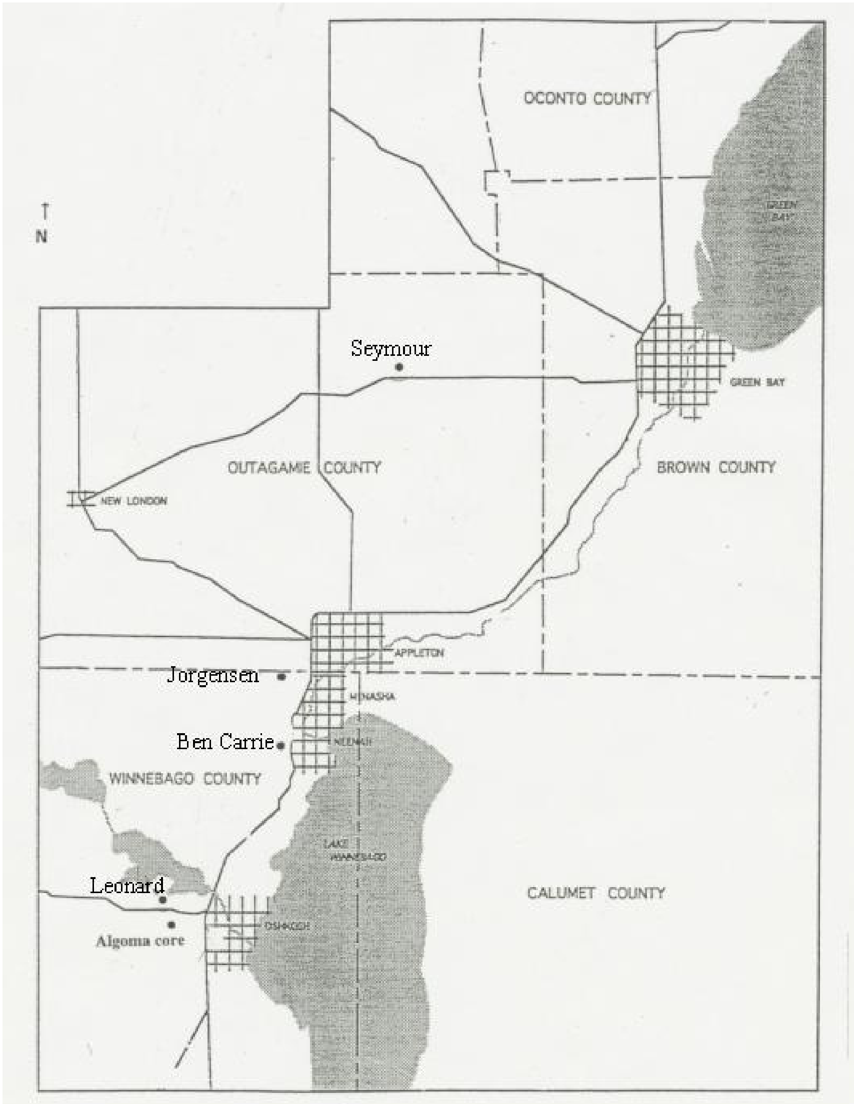

Figure 2. Locations of quarries mapped during project. Algoma core location refers to the Honey Creek field site in the Town of Algoma.

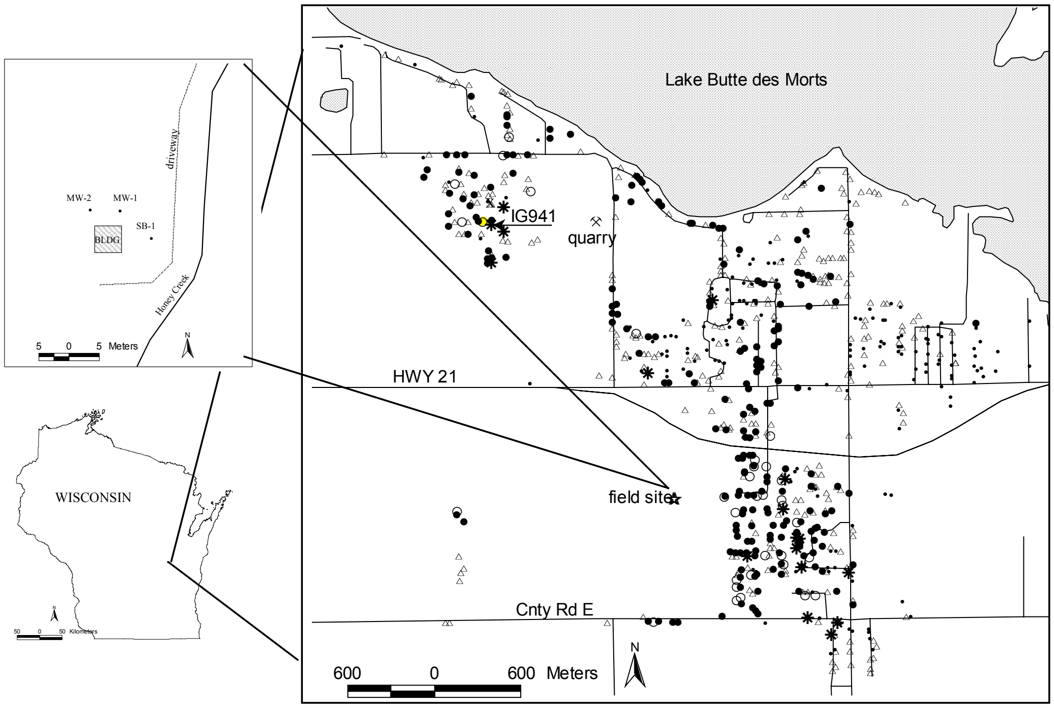

Figure 3. Distribution of arsenic in domestic wells near Honey Creek field site. Inset map shows locations of wells and borings at site. Location of domestic well IG941 and Leonard quarry also shown.

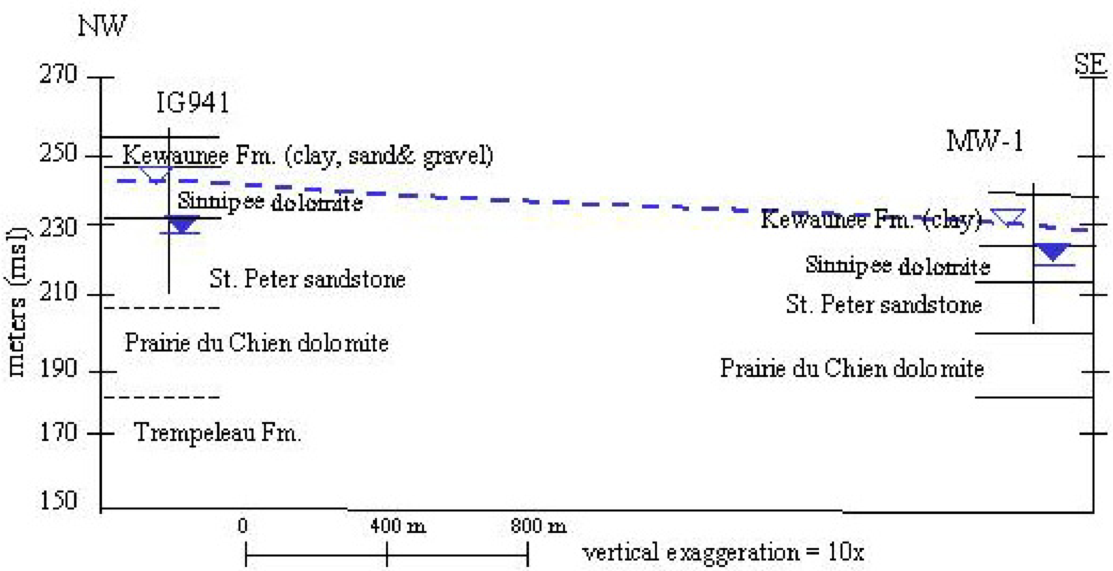

Figure 4. Stratigrphy and water levels at Honey Creek Site and well IG941. Stratigraphy is not continuous in figure because high variability in the thickness of the St. Peter sandstone is expected in this area, based on observations in Leonard quarry, about 800 m west of IG941. Static water levels are shown as open triangles; water levels pumping a a rate of about 57 l/minute are shown as solid triangles.

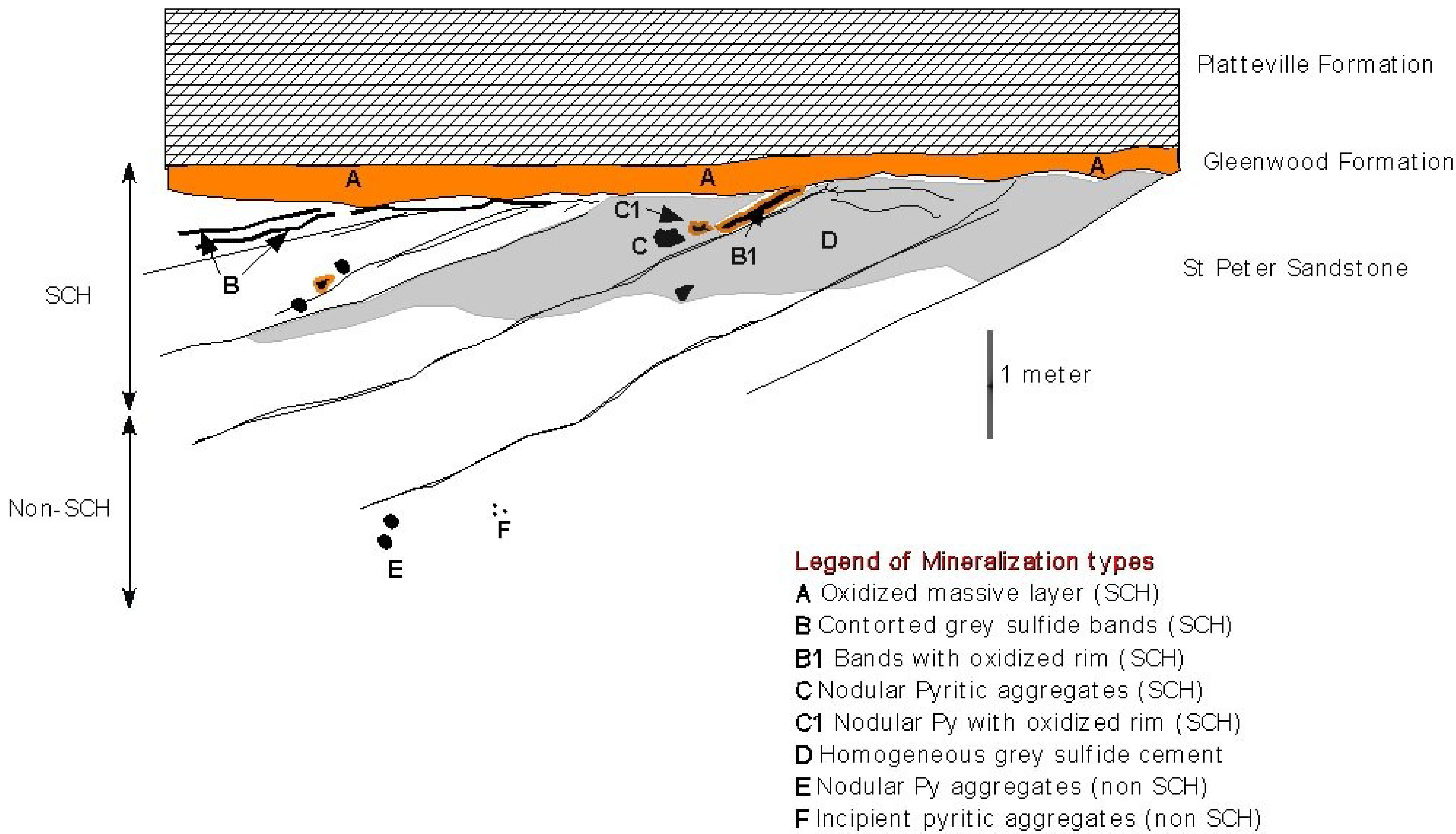

Figure 5. Schematic representation of the stratigrpahic location and types of mineralization in the SCH and non-SCH area

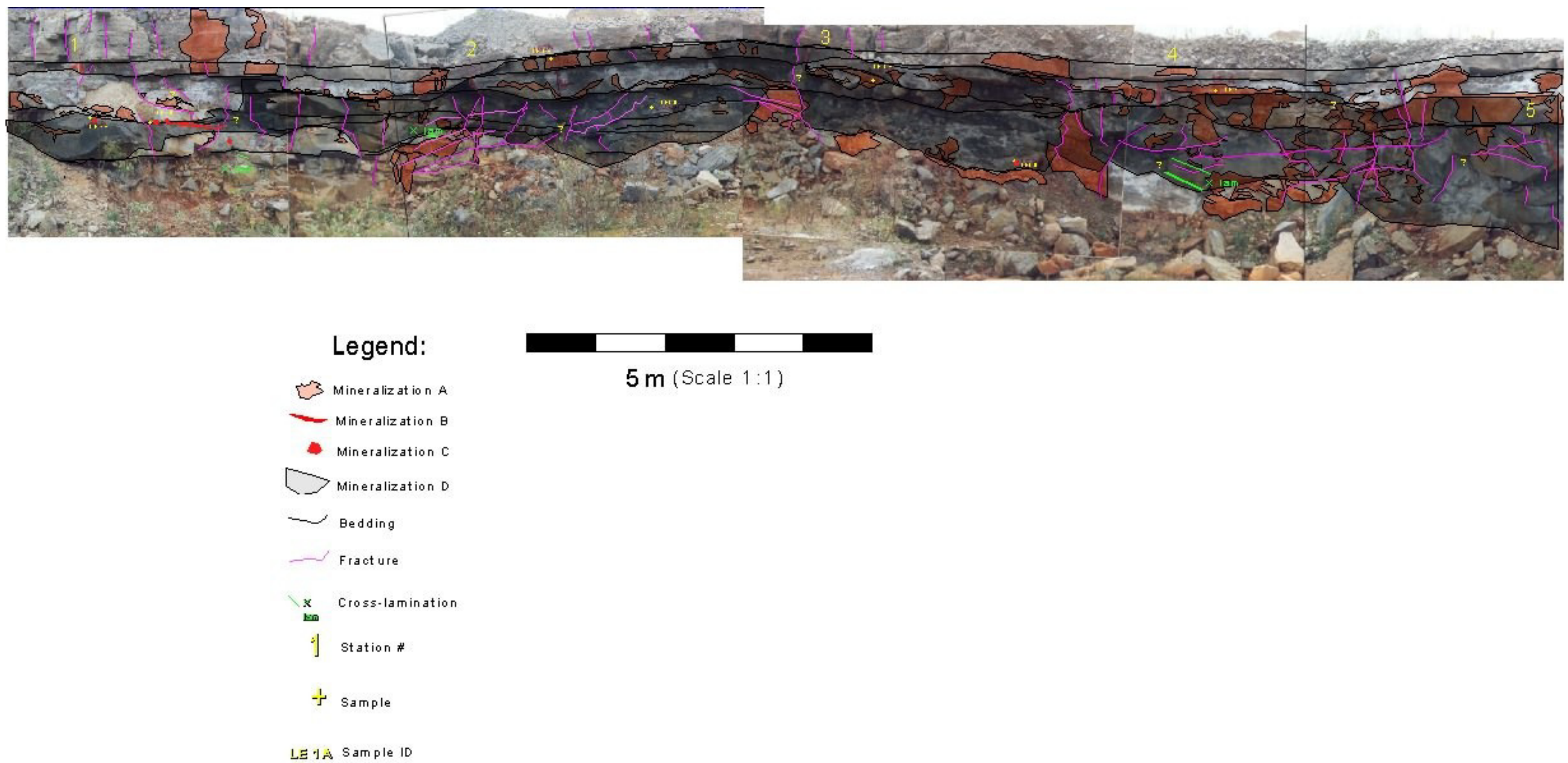

Figure 6a. Photo-mosaic of the east-west wall (wall 1) of Leonard quarry. Formations, bedding, mineralization types, fractures, stations and sample locations are shown.

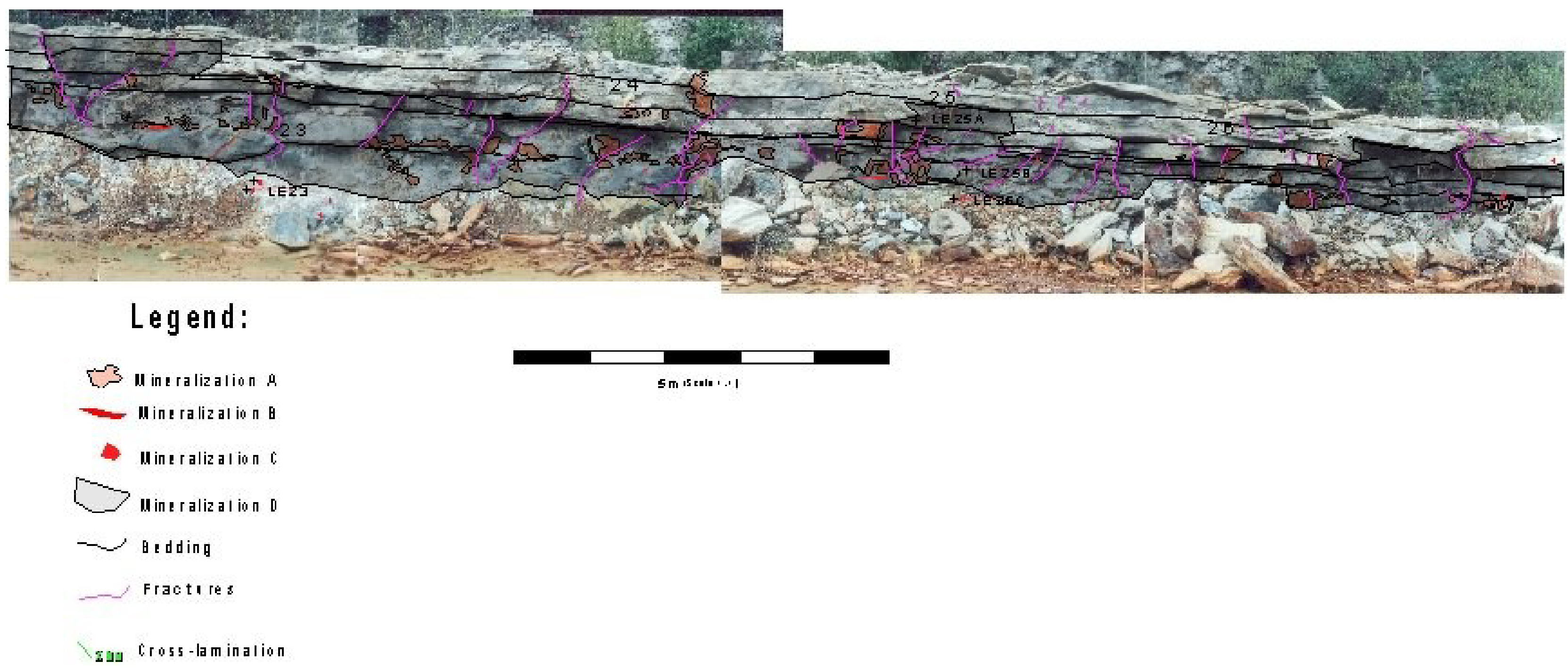

Figure 6b. Photo-mosaic of the north-south wall (wall 2) of Leonard quarry. Formations, bedding, mineralization types, fractures, stations and sample locations are shown.

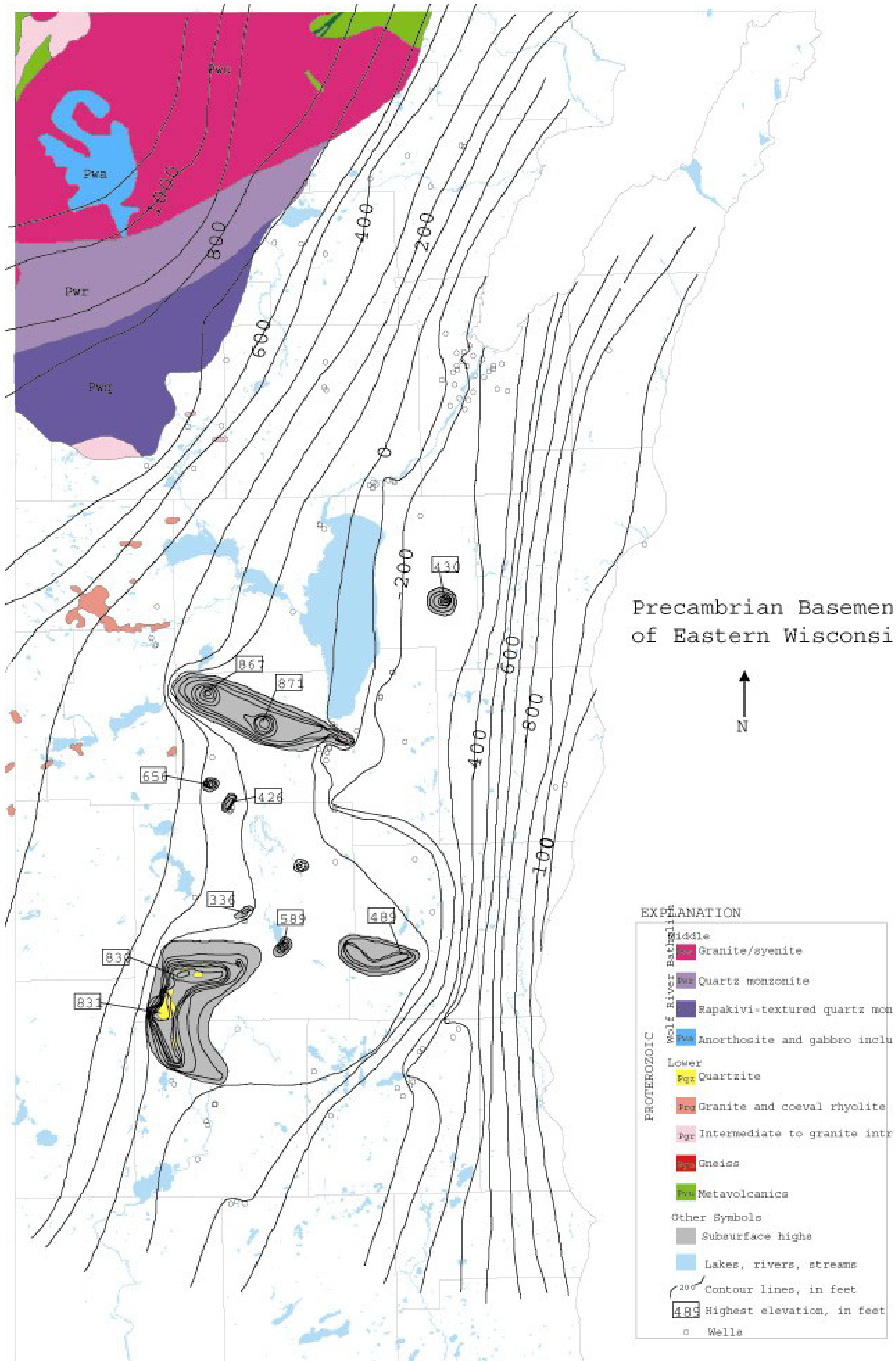

Figure 7. Map of the elevation of the top of the Precambrain basement in eastern Wisconsin.

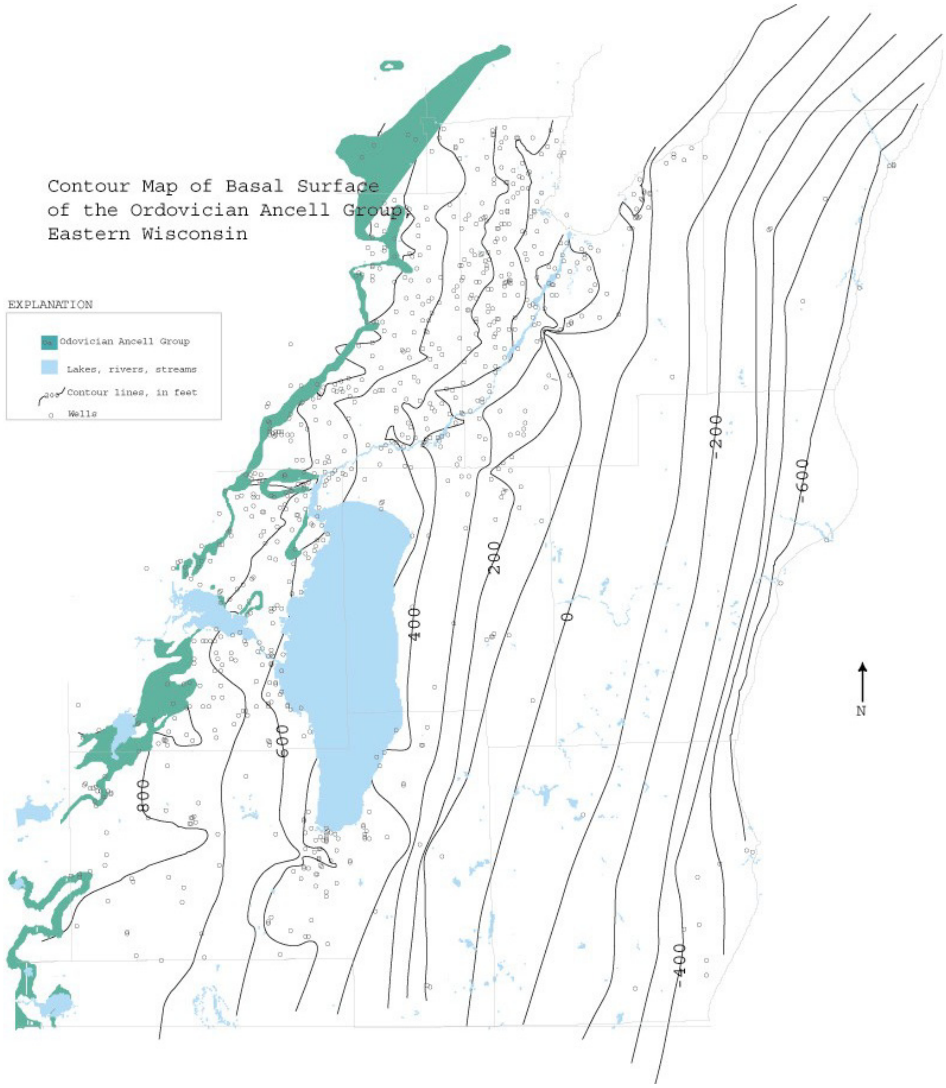

Figure 8. Map of the elevation of the top of the Ancell Group, eastern Wisconsin .

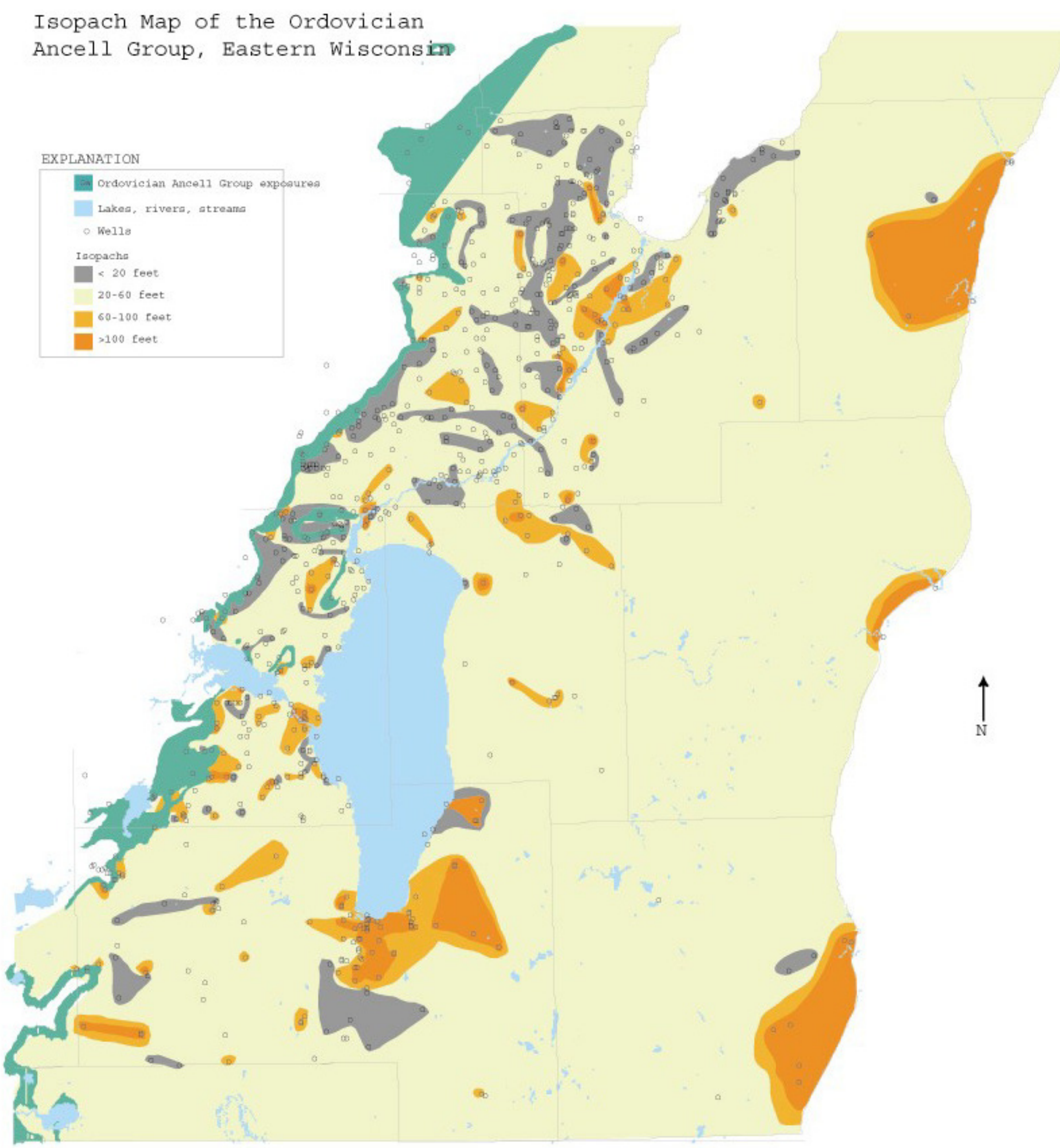

Figure 9. Map of the variation in thickness of the Ancell Group, eastern Wisconsin.

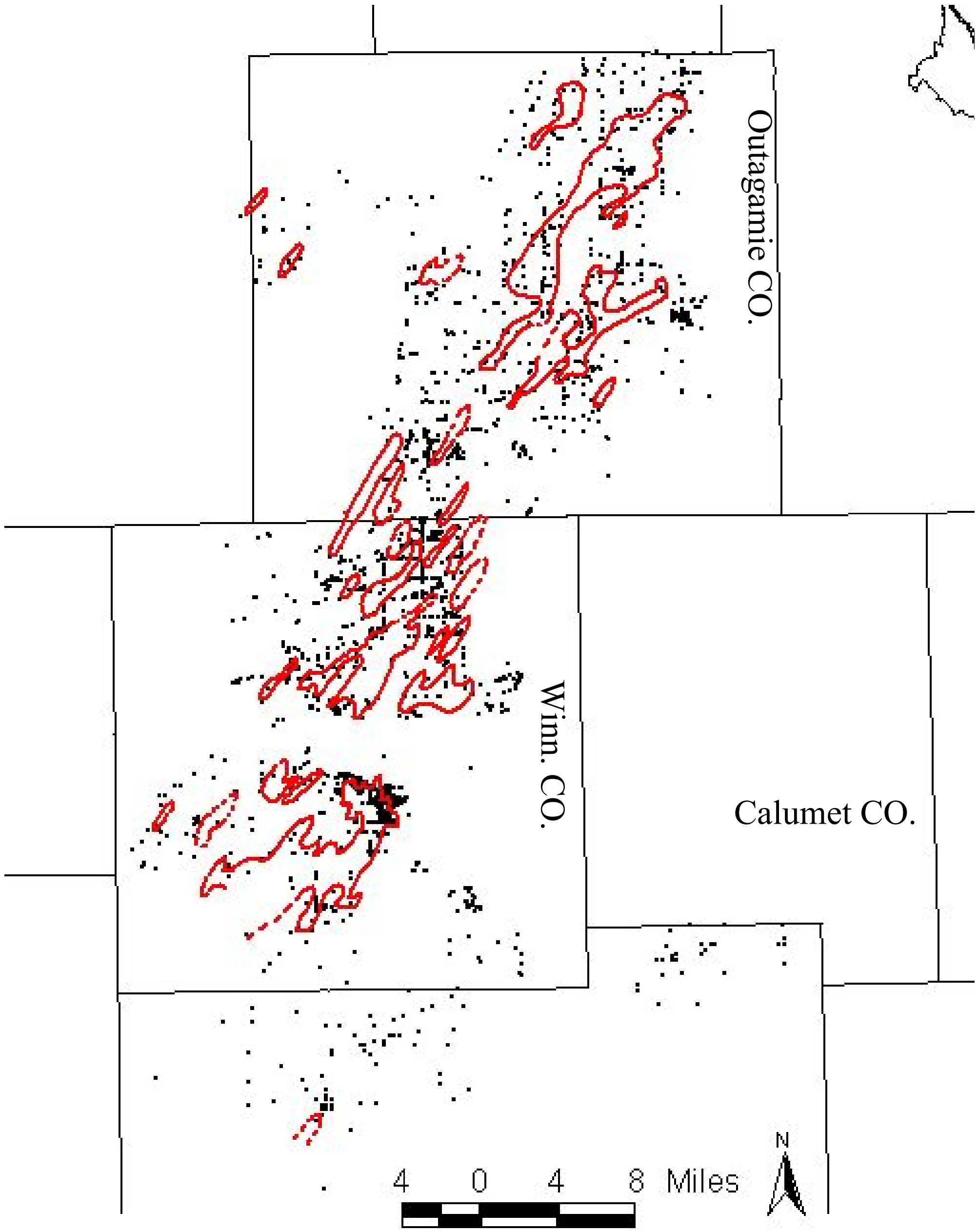

Figure 10. Areas where arsenic concentrations in groundwater exceed 10 µg/L. Areas that exceed 10 µg/L are shown within red contour lines. Based on averaging of results from DNR and Central Wisconsin Groundwater Center town-based sampling data sets. Locations of averaged values shown as black dots.

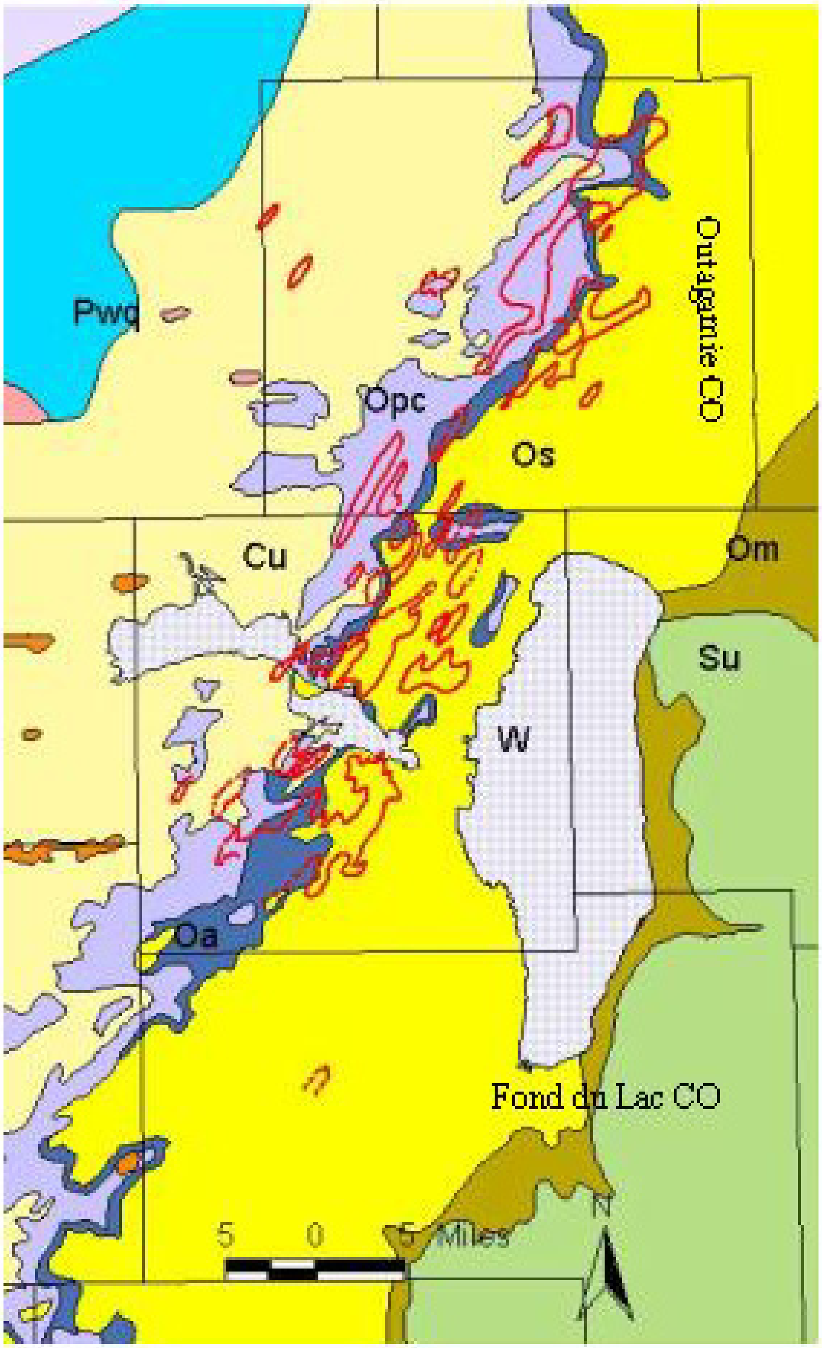

Figure 11. Areas west of the subcrop of the St. Peter sandstone that exceed 10 µg/L arsenic in well water. Cu: undifferentiated Cambrian sandstones; Opc Prairie du Chien Goup; Os Sinnipee Group.

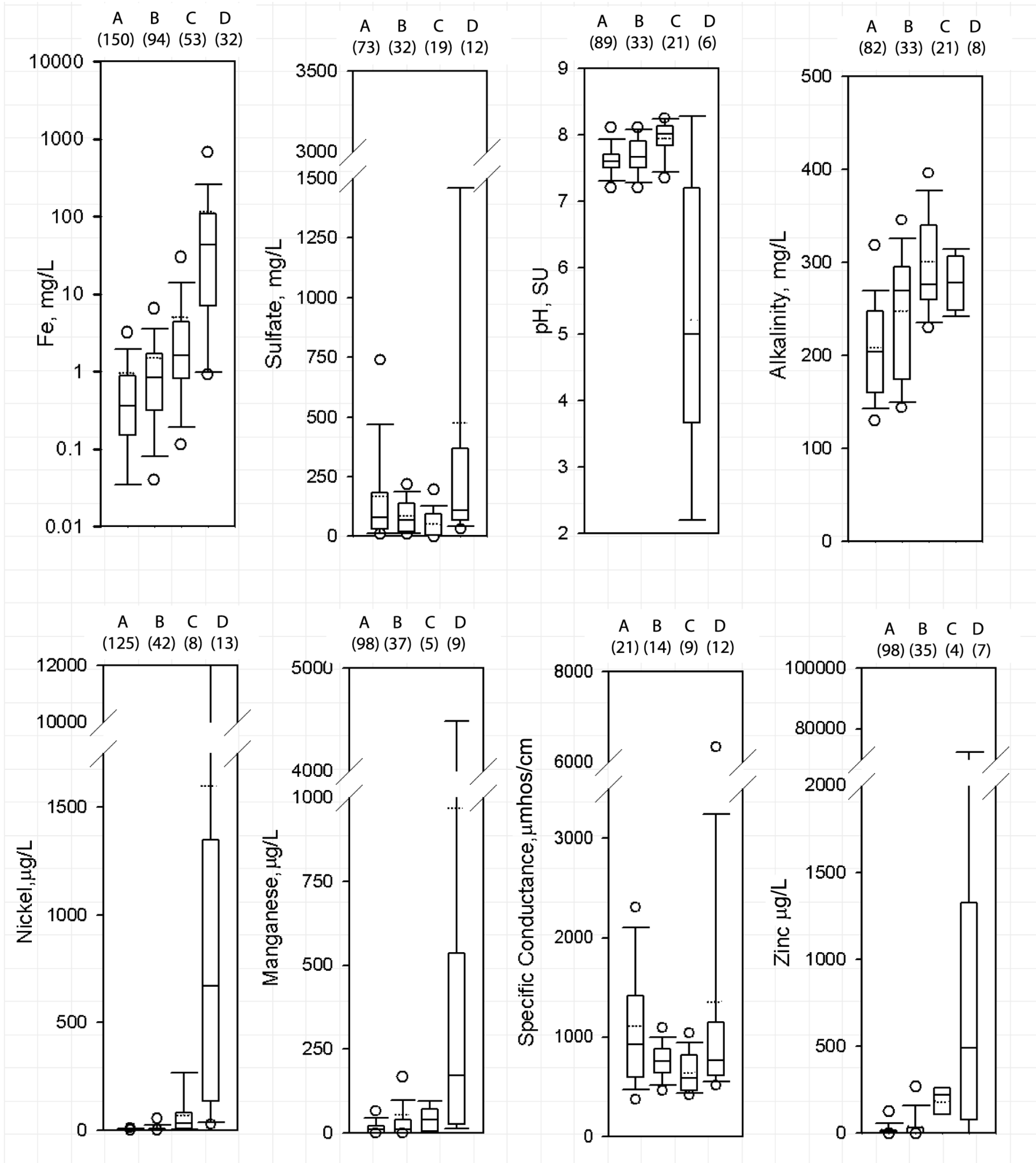

Figure 12. Box plots of concentrations of selected constituents. Plots show the 25th and 75th percentiles as end-lines. Mid-line of the box represents 50th percentile, and capped bars indicate 10th and 90th percentiles. Circles mark 5th and 95th percentiles. The mean value is shown as a dotted line. A, B, C, and D refer to four water types: non-impacted, low, moderate and high arsenic, respectively. Number of samples in parentheses. Data from WDNR GRNs database. Reprinted from Schreiber et al. 2003.

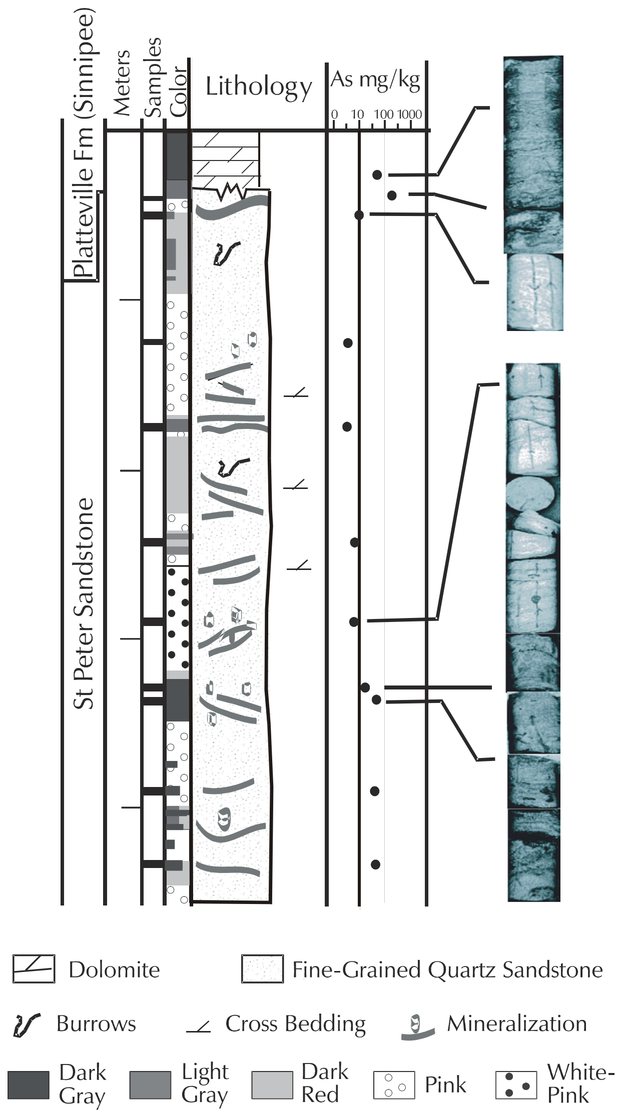

Figure 13a. Lithologic section and description of SB-1 and whole-rock arsenic concentrations (log scale) in mg/kg at selected intervals. Note the high arsenic at the dolomite/sandstone contact and the overall lower (but still elevated) concentrations throughout the St. Peter section. (adapted from Schrieber et al, 2003).

Figure 13b. Photos of core. Upper left: SCH in SB-1. Upper right: nodule and vein with oxidized rim in SB-1. Lower left: SB-1 core, below SCH showing change from oxidized (white to orange) to reduced (gray) sandstone. Mid-right: mineralization in dolomite at 22.3 m (73 feet) below ground surface in MW-1. Lower right: Mineralization with oxidized rim in sandstone.

Figure 13c. Photos of core from SB-1. Labels show arsenic concentration in rock (mg/kg) from sample from that depth.

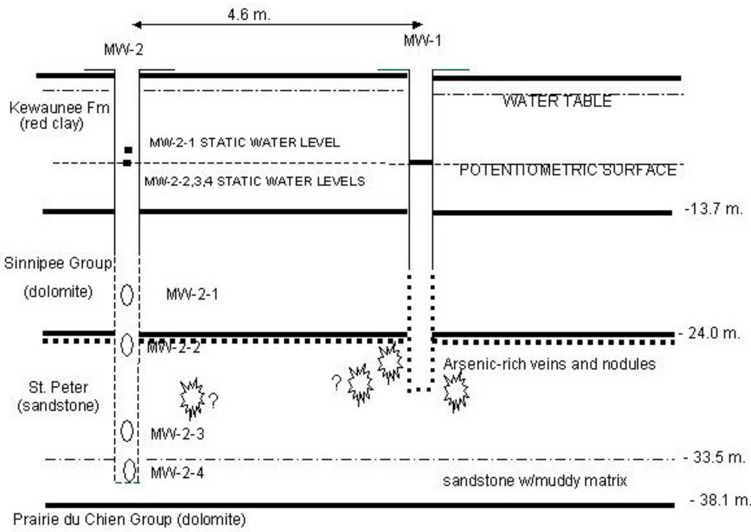

Figure 14. Cross section of Honey Creek site geology, well construction and static water levels. SCH shown as dotted line at dolomite/sandstone contact. Exact locations of arsenic nodules uncertain but were distributed throughout the sandstone cored from the site. Ovals in MW-2 mark depths of four monitoring ports; solid squares indicate head measured at the ports.

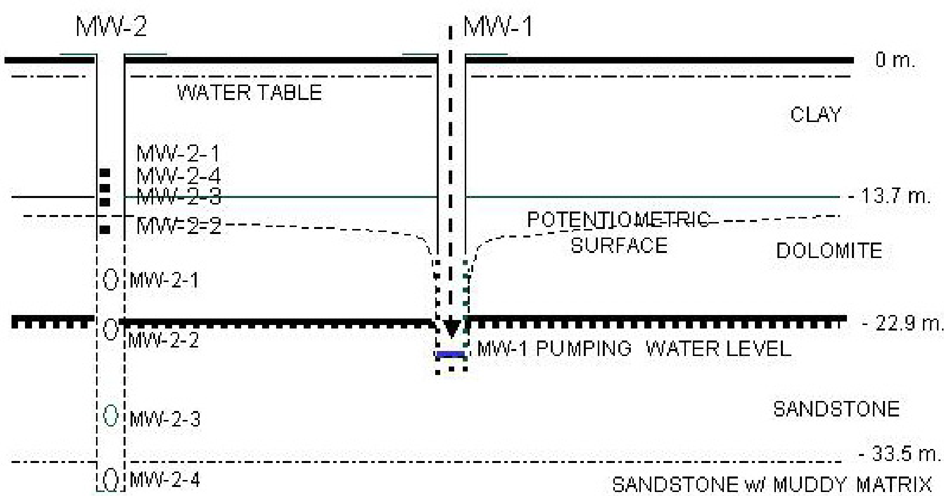

Figure 15. Water levels while pumping from MW-1. Note that the drawdown in MW-1 exposes the SCH (dotted line) to air within the well but does not cause de-watering of the sandstone at MW-2.

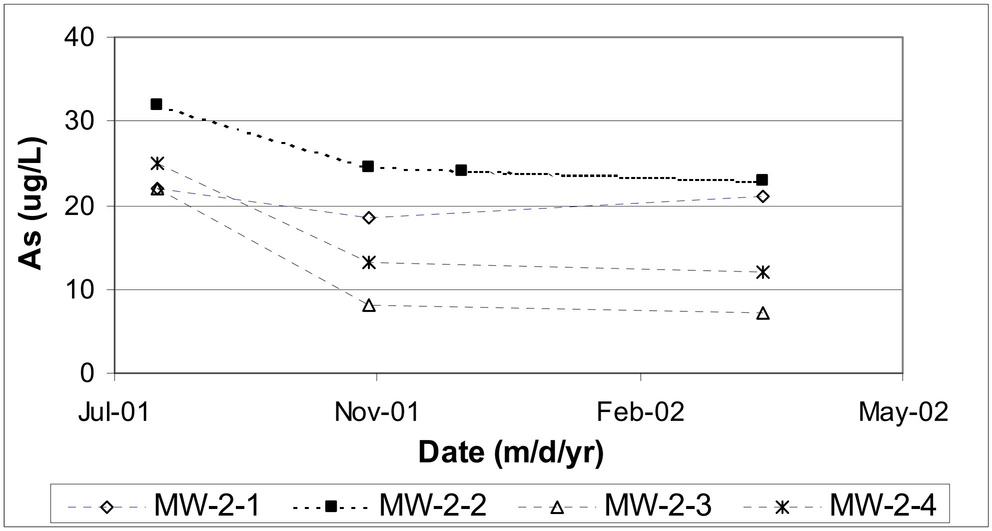

Figure 16. Arsenic concentrations in four ports of MW-2 over time. Elevated and more similar arsenic concentrations during first sampling round may be result of insufficient purging of aquifer following the FLUTe™ installation.

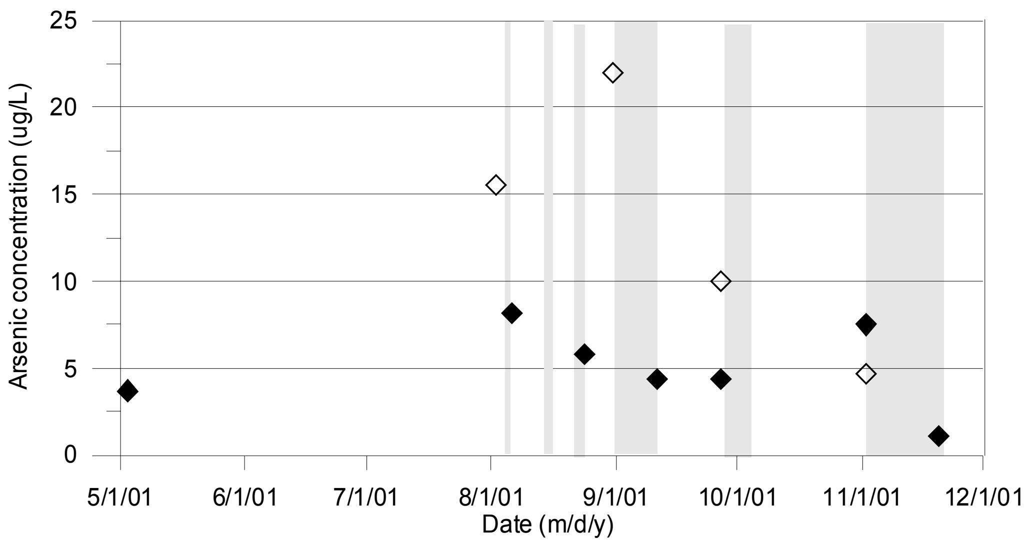

Figure 17. Arsenic concentrations in MW-1 during SCH exposure experiment. Background water quality results are shown prior to 8/2/01. Results during the SCH experiment are shown after 8/2/01. Open diamonds are samples of borehole water, black diamonds are samples aquifer water. Shaded rectangles indicate periods during which pump cycled, exposing the borehole to air.

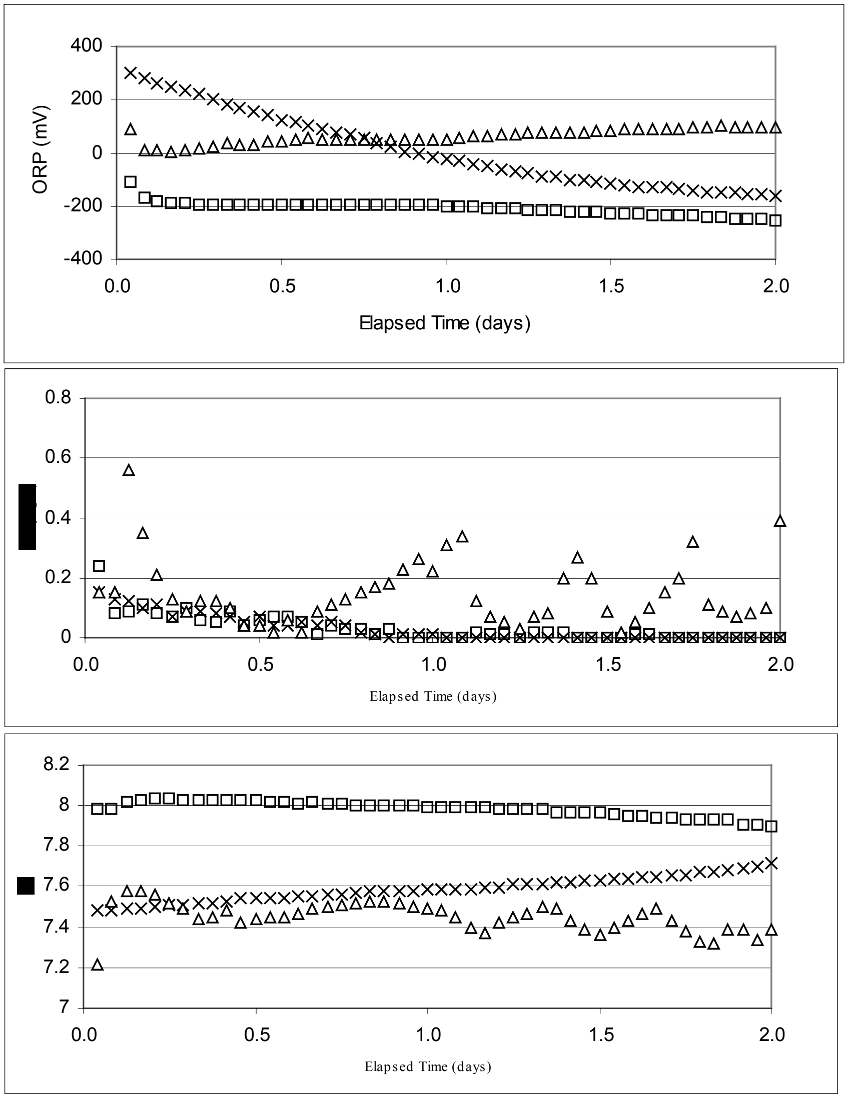

Figure 18. Pumping-induced changes in borehole redox conditions. Hourly measurements collected during background (non-pumping) conditions (squares), a period of pump cycling ten times per hour at 25 gpm (triangles), and a recovery period following cessation of pump cycling (crosses). Frequent pump cycling causes overall elevated Eh, variable DO, and lower pH. After two days of pump shut-off, the borehole returns to close to background, non-pumping conditions.

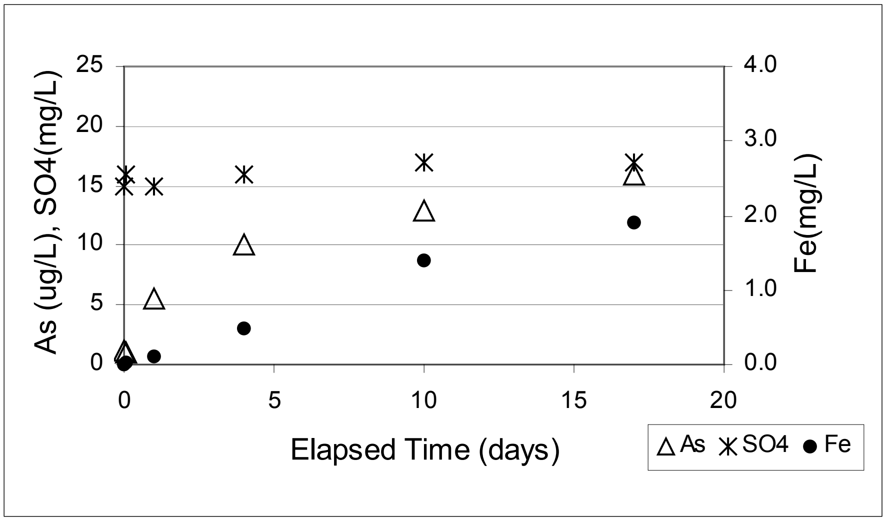

Figure 19. Results of ambient water quality experiment. Arsenic and iron concentrations increase over time. Sulfate is not significantly higher during the test.

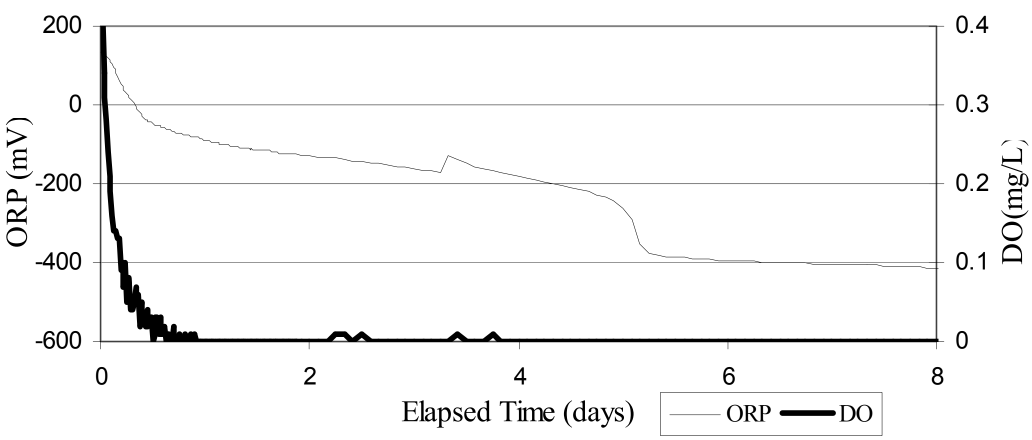

Figure 20. DO and ORP of borehole water during under non-pumping conditions.

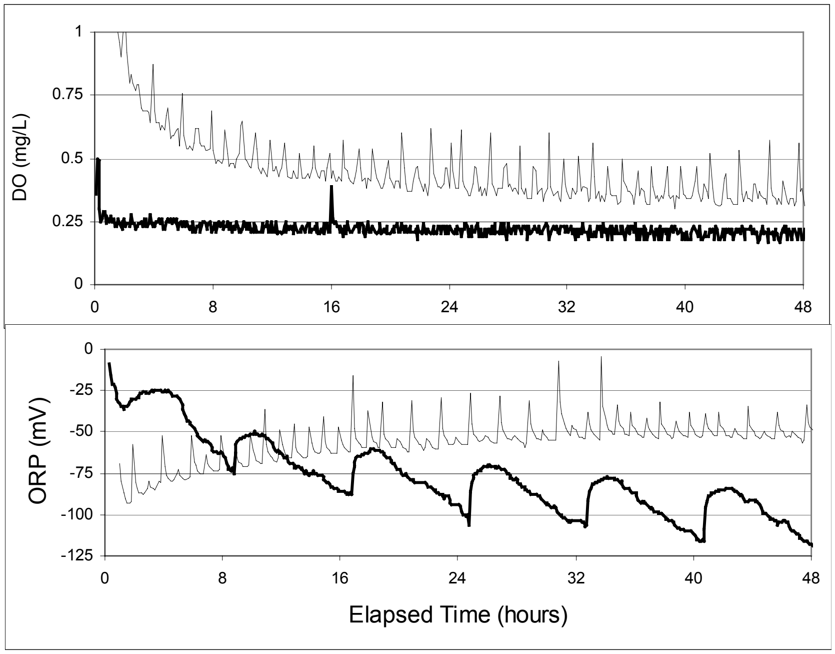

Figure 21. DO and ORP of borehole water during two pumping rates. Dark line in each graph shows conditions pumping at 38 l/min for 10 minutes every 8 hours. Light line shows conditions pumping at 76 l/min for 10 minutes every hour.

Figure 22. Residential development in Town of Algoma simulated in model. Housing density varies from 1 to 2 houses per acre. Red dot shows location of Honey Creek field site.

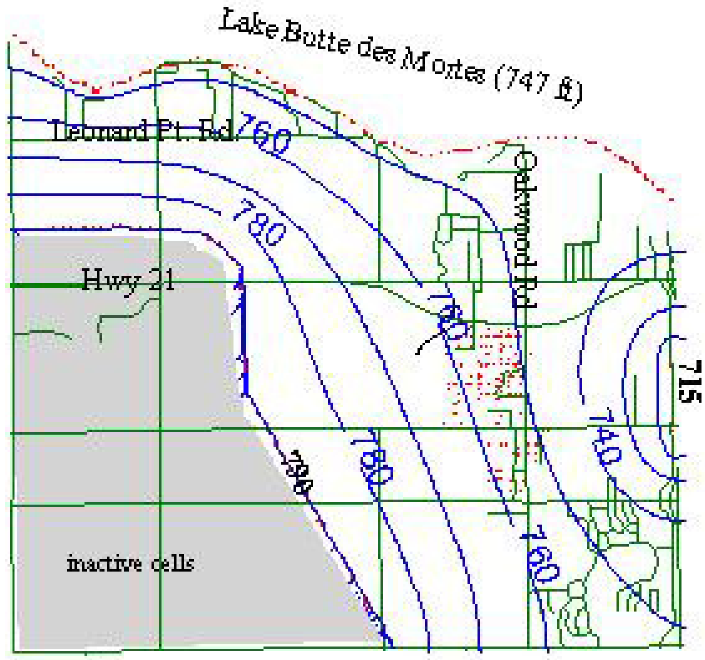

Figure 23. Calibrated potentimetric surface in St. Peter sandstone (top) and drawdown (in feet) predicted by model (bottom). Red symbols show location of wells. Extent of model domain is about 16 square miles.